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PREPRINT

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# SECONDARY AEROSPACE BATTERIES AND BATTERY MATERIALS

## A BIBLIOGRAPHY

G. HALPERT  
W. H. WEBSTER, JR.

AUGUST 1969



— GODDARD SPACE FLIGHT CENTER —  
GREENBELT, MARYLAND

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## PREFACE

This annotated bibliography on the subject of secondary aerospace battery materials and related physical and electrochemical processes was compiled from references to journal articles published between 1923 and 1968. Citations are arranged in chronological order under journal titles. Indices by system, component processes, and author are included.



## INTRODUCTION

A bibliography has been completed on the subject of secondary aerospace battery materials and related physical and electrochemical processes. The majority of space power applications today employ nickel-cadmium, silver-cadmium, and silver-zinc systems. The scope of this bibliography encompasses subjects ranging from metallurgical processes and inorganic preparations to electrochemical and analytical measurements as applied to these systems.

The survey includes technical journal articles published from 1923 through 1968. More than 370 articles and accompanying abstracts were compiled from 40 foreign and domestic journals. Patents and government reports are not included in this publication. The patent literature will be the subject of a future bibliography on this same subject. The NASA and other government reports have been covered recently in a NASA Special Publication (SP-172), "Batteries for Space Power Systems," by P. Bauer.

This publication consists of five parts:

Part I - Index by system and component. Includes both electrochemical system and system components, e.g., nickel-cadmium systems, nickel electrodes, and separators.

Part II - Index by techniques and processes used in the investigations, e.g., analytical, thermal, metallurgical, and kinetic.

Part III - Publication listing. A listing of the forty journals in the order of appearance in this bibliography.

Part IV - Citations and abstracts. Journal titles are arranged in alphabetical order, with the citations and abstracts for the articles in each journal arranged under the journal title, in chronological sequence. The main entry for each citation is the name of the author, which is followed by the volume number of the journal and the page number on which the cited article begins.

Part V - Index by author.

**PART I**

**INDEX BY SYSTEM AND COMPONENT**



## INDEX BY SYSTEM AND COMPONENT

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\* Foreign language journals are indicated in parentheses.



**PART IV**  
**CITATIONS AND ABSTRACTS**

ACADEMIE DES SCIENCES, "COMPTES-RENDUS"

100. Besson, J. 223, 28, (1946)

**Studies Comparing the Anodic Oxidation of Nickel, Cobalt and Manganese in Alkaline Solution.**

The anodic oxidation of nickel, cobalt, and manganese has been the object of much work, but it is impossible to compare the very different experimental conditions. I have proposed to make a study of this phenomena by one unique method with identical conditions for the three metals; a study which is qualitative in order to characterize the definite oxides that are formed.

101. Bagno, O. 236, 1275, (1953)

**The Precipitation of Nickel Hydroxide from Mixtures of Soda and Sodium Carbonate.**

In a preceding note, we have pointed out the retarding action of  $\text{CO}_2$  on the aging of Nickel Hydroxide Solutions. To elucidate on the role of  $\text{CO}_2$ , and in particular the  $\text{CO}_3^{--}$  ion, I have studied the precipitation of  $\text{NiCl}_2$  in mixtures of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .

102. Longuet-Escard, J. and Mering, J. 246, 1231, (1958)

**Abnormal Spacings in Piles of Nickel Hydroxide Molecules having adsorbed  $\text{CO}_3^{--}$  Ions.**

The detection and measurement of abnormal spacings created by the trapping of  $\text{CO}_3^{--}$  ions are performed by way of using an approximate form of Fourier's Set of Reflections.

103. Pacault, A. and Labat, J. 258, 5421, (1964)

**Studies of the Magnetochemistry of Nickel Hydroxide.**

The nickel Hydroxides have been prepared by chemical means, and magnetic studies have been made, in order to be able to analyze the mechanism of the electrochemical oxidation of  $\text{Ni(OH)}_2$  and, consequently, the process of charge and discharge of the positive electrode in alkaline accumulators.



ACTA CRYSTALLOGRAPHICA

200. McMillan, J. A.

7, 640, (1954)

The Crystalline Structure of AgO.

The pattern was obtained with Cu K $\alpha$ , in a universal camera. AgO was prepared by boiling NO<sub>11</sub> Ag<sub>7</sub> with water. Since it was impossible to obtain a single crystal of AgO, we had to interpret the powder pattern.

201. DeWolff, P. M.

21, 432, (1966)

The Crystal Structure of  $\gamma$  Cd(OH)<sub>2</sub>.

A new Cd (OH)<sub>2</sub> phase entirely different from the C<sub>6</sub> type was discovered by Glemser, Hauschild, & Richert, who termed it  $\gamma$  cadmium hydroxide.

AMERICAN CHEMICAL SOCIETY, JOURNAL OF

300. Knobel, M.

45, 70, (1923)

The Activities of the Ions of Potassium Hydroxide In Aqueous Solution.

This work is a revision of that of Chow on the measurement of the electromotive force of concentration cells of potassium hydroxide for the purpose of determining the activities of the ions. Chow's results were based on single measurements for each pair of concentrations and were made with a form of electrode which has since been found to be unreliable.

The principle involved is the same as that used by MacInnes and Parker on potassium chloride solutions, by Ellis, and Noyes and Ellis on hydrochloric acid and by MacInnes and Beattie on lithium chloride. The cells were of the type,  $H_2 | KOH (c_1) | KHg_x | KHg_x | KOH (c_2) | H_2$ , in which the net effect of passing 1 faraday from left to right is the transfer of one mole of potassium hydroxide from a concentration  $C_1$  to a concentration  $C_2$ . The electromotive force is given by the expression,  $E = 2 RT/F \ln a_1 C_1 / a_2 C_2$  where  $a_1$  and  $a_2$  are the mean activity coefficients of the two ions in the two solutions of concentration  $C_1$  and  $C_2$ , respectively; R, T, and F have the usual significance.

301. Cairns R. W., and Ott, E.

55, 527, (1933)

X-Ray Studies of the System Nickel-Oxygen-Water I. Nickelous Oxide and Hydroxide.

Numerous investigators have made x-ray studies of natural and artificial nickelous oxide. The crystal structure has been definitely established as face centered cubic, with a lattice spacing approximately 4.17 Å. The most accurate determinations are probably those of Brentano (4.705 Å.) and Ksanda ( $4.171 \pm 0.003$  Å.). Since both determinations were made with the use of sodium chloride diffraction as a primary standard, there is little doubt as to their accuracy.

302. Cairns, R. W., and Ott, E.

55, 534, (1933)

X-Ray Studies of the System Nickel-Oxygen-Water.

II. Compounds Containing Trivalent Nickel.

1. The existence of compounds having the compositions  $Ni_2O_3 \cdot H_2O$  and  $Ni_2O_3 \cdot 2H_2O$  has been shown. Characteristic x-ray diffraction patterns of these compounds have been obtained.

2. The modes of decomposition of these "hydrates" in water and air at temperatures of 100 to 150° have been established with the aid of x-ray analysis. The results indicated that the compounds were not true hydrates, but contained the water bound as hydroxyl groups. Structural formulas have been assigned.

3. Two compounds of nickel, oxygen and water, at lower stages of oxidation than the above, have been isolated, and their diffraction patterns obtained. Chemical analyses indicated that they were hydrates of the hypothetical oxides  $Ni_3O_4$  and  $Ni_6O_7$ , but their behavior on decomposition showed them to be of a type analogous to the above compounds. Reasonable structural formulas have been proposed.



AMERICAN CHEMICAL SOCIETY, JOURNAL OF (Cont.)

303. Cairns, R. W. and Ott, E. 56, 1094, (1934)

X-Ray Studies of the System Nickel—Oxygen—Water. III. The K-Absorption Limits of Nickel in Various Oxide-Hydrates.

The x-ray absorption limits of various nickel compounds have been studied.

It is shown that a product claimed by us previously to be essentially  $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  contains nickel of a valence higher than two. It is most likely trivalent nickel. This gives further support to our previous conclusions.

304. Tomicek, O., and Freiburger, F. 57, 801, (1935)

Volumetric Determinations in Strongly Alkaline Solutions. I. The Titration of Cobalt with Ferricyanide.

A number of metals have been determined oxidimetrically with ferricyanide, and we wish to present in this communication the direct oxidimetric titration of cobaltous salts by potassium ferricyanide.

305. Akerlof, G., and Bender, P. 63, 1085, (1941)

The Density of Aqueous Solutions of Potassium Hydroxide.

The alkali hydroxides exhibit in many respects a very complex behavior of the greatest interest. To get as clear a picture as possible of their thermodynamic properties in concentrated solutions it is our intention to follow up a previous study of sodium hydroxide with a similar one on potassium hydroxide. With this purpose in mind we will present in this paper some measurements of the density of aqueous solutions of the latter. The "International Critical Tables" (I. C. T.) lists a considerable number of references to such determinations but only one of these seems to give data of higher accuracy at a single temperature. The data referred to are those of Pickering, taken at 15 degrees.

306. Darken, L. S., and Meier, H. F. 64, 621, (1942)

Conductances of Aqueous Solutions of the Hydroxides of Lithium, Sodium and Potassium at 25°.

Previous work done in this Laboratory on the conductance of acids and salts led to the belief that the application of this same conductance method to the hydroxides of lithium, sodium, and potassium would give information as to whether these bases behaved as typical strong electrolytes or whether they exhibited evidence of incomplete ionization.

The conductances were measured using the same apparatus and technique described in previous publications. The values of Jones and Bradshaw for the specific conductivities of potassium chloride solutions were used to determine the cell constants.

AMERICAN CHEMICAL SOCIETY, JOURNAL OF (Cont.)

307. Akerlof, G. C., and Bender, P. 70, 2366, (1948)

Thermodynamics of Aqueous Solutions of Potassium Hydroxide.

The results presented in this paper represent a continuation of a program of studies of the thermodynamic properties of concentrated aqueous electrolytic solutions in which measurements on hydrochloric acid and sodium hydroxide solutions have already been reported. A detailed description of the experimental procedure and the method of calculation employed here has been given previously. In the following all symbols agree with common usage or with those in earlier papers.

308. Gayer, K. H., and Garrett, A. B. 71, 2973, (1949)

The Equilibria of Nickel Hydroxide  $\text{Ni}(\text{OH})_2$  in solutions of Hydrochloric Acid and Sodium Hydroxide at 25 degrees.

The purpose of this investigation was to obtain data on the equilibria of nickel hydroxide in dilute solutions of sodium hydroxide and hydrochloric acid. Such data make possible (1) the determination of the character of the ions in dilute solutions, (2) the evaluation of the free energy of formation of these ions, (3) the evaluation of the solubility and the solubility product of nickel hydroxide, and (4) the amphoteric nature of the hydroxide.

Previous work on nickel hydroxide is at variance as to the magnitude of the water solubility and the solubility product. Almkvist reported the solubility of nickel hydroxide to be  $1 \times 10^{-4}$  mole at 20 degrees. Britton calculated the solubility product to be  $2.07 \times 10^{-17}$  at 25 degrees; while Wijs reported a value of  $1.6 \times 10^{-14}$ .

No work is reported which can be used to show the complete record of the behavior of nickel hydroxide in acid and basic solutions; data for that record are presented in this paper.

309. Dyer, L. D., Borie, B. S., Smith, G. P. 76, 1499, (1954)

Alkali Metal-Nickel Oxides of the Type  $\text{MNiO}_2$ .

This article describes the preparation and properties of two compounds of trivalent nickel which have not previously been isolated. The compounds sodium nickelate (III),  $\text{NaNiO}_2$ , and lithium nickelate (III),  $\text{LiNiO}_2$ , were prepared by bubbling oxygen through sodium hydroxide and lithium hydroxide, respectively, contained in nickel tubes at about  $800^\circ$ . The crystals obtained upon removing the top section of the cooled melt were washed with absolute ethyl alcohol to remove the hydroxide. The sodium compound was also prepared by heating a one to three mixture of sodium peroxide and sodium hydroxide in a nickel tube and treating as described above. Lithium nickelate (III) is rhombohedral with the cesium dichloriodide,  $\text{CsCl}_2\text{I}$ , structure.

AMERICAN CHEMICAL SOCIETY, JOURNAL OF (Cont.)

310. Carriel, J. T., and Singley, W. J.

76, 3839, (1954)

Composition of Basic Nickel Carbonates.

Basic nickel carbonates were formed at constant pH and room temperature by the addition of standard nickel chloride and potassium hydroxide solutions to a reaction medium containing a 10-fold excess of potassium carbonates. The composition of the precipitates may be expressed  $\text{Ni(OH)}_2 \cdot 3$  to  $4 \text{ NiCO}_3$  in the pH range 8 to 10.5; above pH 10.5 the ratio of carbonate to hydroxide in the precipitate decreases rapidly. Essentially no chloride is absorbed by the precipitate. A previously developed method of precipitation at constant pH was adapted to permit calculation of the composition of the precipitate directly from buret readings.



## ANALYTICAL CHEMISTRY

400. Brummet, B. D., and Hollweg, R. M. 28, 887, (1956)

### Determination of Nickel in Oxidized Films on Nickel Metal.

A rapid spectrophotometric method for the determination of nickel in oxidized films on nickel metal has been developed. The solvent used 0.5% potassium cyanide, dissolves the oxidized film but not the nickel metal. The method is sensitive to microgram quantities of nickel.

401. Lauer, G., Abel, R., and Anson, F. C. 39, 765, (1967)

### Electrochemical Data Acquisition and Analysis System Based on a Digital Computer.

A system is described in which a small digital computer is programmed to initiate an electrical experiment, to acquire, digitize, and store electrochemical data, to test for completion of a run, and to perform a functional analysis on the stored data. Experiments are described whereby the apparatus was used to study adsorbed reactants by the chronocoulometric technique. Examples are given of other electrochemical experiments in which the computer-based system will afford major improvements in the quality of data acquired and in the speed of data reduction.

402. Orr, C., Jr. 39, 834, (1967)

### Specific Surface Area by Low Pressure Permeametry.

The present work describes a flow apparatus and a technique of operation at progressively lower pressures; the technique achieves specific surface area results that are in remarkably close agreement with low temperature gas adsorption (BET) values for the same material.



## ANNALES DE CHEMIE

500. Cabannes—Ott, C.

5, 905, (1960)

### Concerning the Constitution of some Metal Oxide Hydrates (Thermogravimetry and Infrared Spectroscopy).

When one treats a metallic salt with a basic material, one considers generally that the product obtained is a hydrated oxide or a basic salt more or less well defined. The oxide can associate itself with a given number of water molecules. It can form a gel of a poorly established hydration or it can present itself in a form of a hydroxide in which the water is a part of the constitution of the material in the form of oxydriles. Furthermore, it is well known that, besides the possible formation of basic salts, the hydrated oxides retain the ions in whose presence they find themselves during the preparation and thus find it quite difficult to separate themselves.

501. Labat, J.

9, 399, (1964)

### Contribution to the Studies of Nickel Hydroxide.

We have demonstrated in a preceding article the extent of difference in opinion of various authors on the nature and the very existence of oxides and hydroxides of nickel with valences greater than two; despite a considerable amount of research on their composition structure, no systematic research has yet been conducted on their magnetic properties. We shall mention only the work of Miss Veil on their evolution – when immersed in water – of the nickel hydroxide and of the hydrate of nickel sesquioxide, the results obtained by Bhatangar and Bal which agree on the existence of the definite NiO oxide and, finally, the recent short thermomagnetic study of  $\text{Ni}_2\text{O}_3\text{H}_2\text{O}$  made by Richardson.

Without any doubt, this investigation method should be particularly interesting as the oxidation degree directly related to the valence of the nickel in these compounds must evidently affect their magnetic characteristics. For this reason we have undertaken a study of magnetism in these oxides, their chemical analysis, the X-ray spectrum and their electrochemical properties depending upon the method used in their preparation.

## ANORGANISCHE CHEMIE, ZEITSCHRIFT FÜR

600. Glemser, O., and Einerhand, J.

261, 26, (1950)

### Higher Nickel Hydroxides

Through Calorimetric Titrations, higher Nickel hydroxides were found to be  $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ ,  $\text{Ni}_2\text{O}_3 \cdot x \text{H}_2\text{O}$  and  $\text{Ni}_3\text{O}_4 \cdot x \text{H}_2\text{O}$ . From the oxidation also arises the primary product  $\text{NiO}_2 \cdot x \text{H}_2\text{O}$  which forms with  $\text{Ni(OH)}_2$ ,  $\text{Ni}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ ;  $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$  reacts with  $\text{Ni(OH)}_2$  to  $\text{Ni}_3\text{O}_4 \cdot x \text{H}_2\text{O}$ .  $\text{NiO}_2$  is x-rayed and decomposes slightly.

601. Glemser, O., and Einerhand, J.

261, 43, (1950)

### The Structure of Higher Nickel Hydroxides.

The structure of the new higher nickel hydroxides discovered in the preceding work is determined by evaluation of roentgen photographs; electronoptical photographs are also employed for supporting the finding.

## ANORGANISCHE UND ALLGEMEINE CHEMIE, ZEITSCHRIFT FÜR

700. Hüttig, G. F., and Peter, A.

189, 183, (1930)

### Contribution to the Knowledge of Oxide Hydrates. XXIV. The Nickel (II) Oxide/Water System.

With these preparations, there is no action by the oxygen of the air, but the carbon dioxide of the air could have some influence. For this reason, the various operations (precipitation, decanting, filtration, washing) were conducted in the same, although occasionally somewhat simplified arrangement as described by G. F. Hüttig and R. Kassler (oxide hydrates XXI; 1. c.). Instead of illuminating gas, air free of carbon dioxide was passed through the apparatus here. Filtration was accomplished with a Zsigmondy membrane filter, and the precipitate was protected against the action of atmospheric air in the same manner as described in the reference.

701. Feitknecht, W., Christen, H. R., and Studer, H.

283, 88, (1956)

### Knowledge of the Higher Nickel Hydroxides; the Oxidation of Nickel Hydroxide.

The higher nickel hydroxide formulated by Glemser and Einerhand as  $\text{Ni}_3\text{O}_2(\text{OH})_4$  has a disordered layer structure with rhombically deformed layers and an average nickel ion interval which lies between  $\text{Ni}(\text{OH})_2$  and B-NiOOH. Its homogeneity range extends up to the composition NiOOH.

The oxidation of nickel hydroxide takes place strictly topochemically. Under certain conditions, the composition can also become NiOOH with retention of the lattice. In addition, contraction of the layers with formation of the lattices of  $\text{Ni}_3\text{O}_2(\text{OH})_4$  and possibly B-NiOOH takes place.

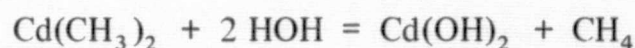
The oxidation products of nickel hydroxide are, with the same composition, different from those obtained by oxidation of nickel ions in alkaline media.

702. Glemser, O., Hauschild, U., Richert, H.

290, 58, (1957)

### A New Polymorphic Modification of Cadmium Hydroxide.

The hydrolysis of cadmium alkylene is described. According to



for example, cadmium methyl hydrolyzes in 96% ethanol at  $-10$  to  $0^\circ\text{C}$  to  $\gamma\text{-Cd}(\text{OH})_2$ , a new crystalline modification of cadmium hydroxide. Density  $d_4^{25} = 4.81 \text{ g/cm}^3$ ; solubility  $1.2 \cdot 10^{-5} \text{ mol/l}$ . When heated with water to  $150^\circ$  in a pressure vessel,  $\gamma\text{-Cd}(\text{OH})_2$  changes within 4 days to coarsely crystalline B- $\text{Cd}(\text{OH})_2$  [C6 type]. In a vacuum, the new hydroxide decomposes at  $p_{\text{H}_2\text{O}} = 10 \text{ torr}$  at  $115^\circ$  to  $\text{CdO}$  and  $\text{H}_2\text{O}$ . Ultraphotographs suggest hydrogen bridge formations. A shortest O-O interval of  $2.74 \text{ \AA}$  and various Cd-O intervals, 1. Cd-O =  $2.37 \text{ \AA}$ ; 2. Cd-O =  $2.40 \text{ \AA}$ , are calculated from the absorption bands observed. In the case of  $\gamma\text{-Cd}(\text{O})$ , it is possible to detect bending vibrations ( $\delta$ ) of the hydrogen of the OH group.



APPLIED CHEMISTRY OF THE U.S.S.R., JOURNAL OF  
(English Translation)

800. Vasserman, I. M., Fomina, E. A.

34, 84, (1961)

Investigation of Chemical Aging and of the Anomalous Aging of Precipitates Induced by it,  
in the Case of Basic Nickel Carbonate.

The communications cited dealt with studies of chemical and anomalous aging of precipitates in the  $\text{Ni}(\text{NO}_3)_2 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$  system, mainly from the qualitative aspect. Chemical precipitation in this system, is a particular case of the precipitation of sparingly soluble basic salts. It follows that the results obtained in the study of the system are of general significance for all this group of precipitates.

In the present investigation we continued the study of chemical and anomalous aging of precipitates in the  $\text{Ni}(\text{OH})_2 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$  system, from the qualitative aspect. Of the five types of secondary chemical reactions specified earlier, two take place in this system: 1) neutralization of the basic precipitate (basic nickel carbonate) with an acid salt (sodium bicarbonate), present in the mother liquor: 2) hydrolysis of the basic precipitate.

The purpose of the present work was to study these reactions and their kinetics. For comparison, ordinary aging of basic nickel carbonate was studied together with its anomalous aging.

## CANADIAN JOURNAL OF CHEMISTRY

900. Lang, A. A., and Sukava, A. J. 36, 1064, (1958)

### The System $\text{KOH}-\text{K}_2\text{CO}_3-\text{H}_2\text{O}$ at Low Temperatures. I. Phase Equilibria.

Phase diagrams for the system  $\text{KOH}-\text{K}_2\text{CO}_3-\text{H}_2\text{O}$  were determined for  $25^\circ$ ,  $10^\circ$ ,  $0^\circ$ ,  $-10^\circ$ ,  $-20^\circ$ ,  $-40^\circ$ , and  $-60^\circ$ . The stable hydrates of potassium hydroxide were the di- and tetrahydrates; those of potassium carbonate were the sesqui- and hexa-hydrates. No compound formation between  $\text{KOH}$  and  $\text{K}_2\text{CO}_3$  was detected.

901. Lake, P. E., and Goodings, J. M. 36, 1089, (1958)

### The Nature of The Cadmium Ions in Hydroxide and Carbonate Solutions.

The nature and concentration of the cadmium-containing ions in potassium hydroxide and potassium carbonate solutions have been studied polarographically. The co-ordination number for the hydroxide-cadmium complex is 4 and its dissociation constant  $2 \times 10^{-10}$ . The co-ordination number for the carbonate-cadmium complex is 3 and its dissociation constant  $6 \times 10^{-7}$ .

902. Conway, B. E., and Bourgault, P. L. 37, 292, (1959)

### The Electrochemical Behavior of The Nickel-Nickel Oxide Electrode Part I. Kinetics of Self Discharge.

The nickel-nickel oxide electrode forms the positive plate in the charged nickel-cadmium battery. After "charging" the electrode to a chemical state represented by the non-structural formula  $\text{NiO}_x$  where  $x$  can vary from about 1.4 to 1.8 depending on the current density and temperature, loss of oxygen and a fall of potential on open circuit occurs. In the present work this "self-discharge" effect has been examined by study of (i) the rate of decay of e.m.f. on open circuit, (ii) rate of oxygen evolution on open circuit, (iii) the electrochemical capacity of the electrode, and (iv) the build-up or charging curves for the electrode. The decay behavior has been studied in aqueous  $\text{KOH}$  solutions from 0.0015 to 15 M. Tafel slopes are obtained from the plots of e.m.f. vs.  $\log$  (time of decay), and abrupt changes occur at certain electrode potentials which indicate changes of rate-determining mechanism in the self-discharge process. The slopes observed are interpreted in terms of a new scheme of consecutive reactions for anodic oxygen evolution by deducing, by means of the Christiansen method, the relevant Tafel slopes. It is shown that the scheme proposed uniquely accounts for the experimental behavior and that the change of mechanism observed in the self-discharge can only be explained if two consecutive and not alternative processes are invoked. The dependence of the rates of self-discharge upon  $\text{OH}^-$ -ion and water activity is deduced and the significance of these results is discussed.



CANADIAN JOURNAL OF CHEMISTRY (Cont.)

903. Bourgault, P. L., and Conway, B. E.

38, 1557, (1960)

The Electrochemical Behavior of  
The Nickel Oxide Electrode Part II. Quasi-Equilibrium Behavior.

The electrode potential of the nickel oxide electrode has been determined as a function of water and solute activity in aqueous solutions of potassium hydroxide. The electrode, which was charged to a mean state of oxidation corresponding to 50% Ni II and 50% Ni III, was examined after long periods of time and by cathodic and anodic e.m.f. decay measurements after polarization in order to establish the quasi-reversible potentials by two methods. The results are discussed in terms of the stoichiometry of the potential-determining reaction, and distinction between mixed and true reversible potentials is made.

904. Conway, B. E., and Bourgault, P. L.

40, 1690, (1962)

Electrochemistry of The Nickel Oxide Electrode Part III.  
Anodic Polarization and Self Discharge Behavior.

Further evidence that the rate-controlling process in self discharge of the nickel oxide electrode is the anodic partial reaction of oxygen evolution is reported and is based on: (a) comparison of the heats of activation for open-circuit oxygen evolution and for d.c. anodic polarization with oxygen evolution: (b) comparison of the current potential behavior for d-c anodic polarization and for rates of oxygen evolution on open circuit as a function of potential: and (c) comparison of H/D isotope effects for open-circuit and d.c. polarization behavior. In the latter cases, an unusual and characteristic inverse isotope effect is observed.

True Tafel slopes are deduced and interpreted in terms of possible mechanisms of oxygen evolution, taking account of the dependence of activation energy upon surface coverage by adsorbed intermediates.

905. Conway, B. E., and Gileadi, E.

40, 1933, (1962)

Electrochemistry of the Nickel Oxide Electrode.  
Part IV. Electrochemical Kinetic Studies of Reversible Potentials  
as a Function of Degree of Oxidation.

Electrochemical kinetic studies have been carried out at the nickel oxide electrode showing that the reversible potential for the  $\text{Ni}^{\text{II}}-\text{Ni}^{\text{III}}$  system is independent of the state of oxidation of the bulk oxide in the electrode over a wide range of degrees of oxidation. The properties of the electrode are shown to be determined by the state of a surface phase, which is completely charged when the bulk oxide material in the electrode has been charged to 10% of its total charge capacity. Experiments on sparingly charged electrodes have proved that charging of the bulk oxide does not commence significantly until the electrode is charged to about 1.5%. Consecutive electrochemical reactions possibly involved in the charging process are discussed.

909. Casey, E. J., and Moore, W. J.

43, 1199, (1965)On The Formation of " $\text{Ag}_2\text{O}_3$ " on Silver Electrodes.

" $\text{Ag}_2\text{O}_3$ " was examined electrochemically in cutectic  $\text{KOH}-\text{H}_2\text{O}$  at  $-40$  degrees C by coulombic measurements of quantities formed, open circuit potential decays, variation of potential as a function of anodic current density, and temperature coefficients of decomposition rates. It can be formed directly from  $\text{Ag}_2\text{O}$  on Ag at current density (c.d.)  $> 15\mu\text{A}/\text{cm}^2$ , with a maximum thickness during the first oxidation cycle (25 layers, assuming a surface roughness factor of one) occurring at  $65\mu\text{A}/\text{cm}^2$ . Potential decay ( $-\partial E/\partial \log t \equiv b$ ) curves have protracted linear regions where  $0.045 < b < 0.078$ , sometimes higher. One-tenth of a layer of adsorbed species superimposed on the higher oxide exists on the surface during  $\text{O}_2$  evolution. Reduction curves show a minimum in the potential decay of the higher oxide preceding the formation of  $\text{Ag}_2\text{O}$ . The " $\text{Ag}_2\text{O}_2$ " decomposes in approximately 1 h at  $-40$  degrees C to either AgO or  $\text{Ag}_2\text{O}$ . The activation energy for its thermal decomposition is  $12.0 \pm 2.0$  kcal/mole. Under most experimental conditions studied, the results indicated that the material is not true  $\text{Ag}_2\text{O}_2$  but it is probably better described as  $\text{Ag}_2\text{O}[\text{O}]$  where  $[\text{O}]$  is trapped oxygen.

The evidence does point to the probable existence of a thin layer, which may be true  $\text{Ag}_2\text{O}_2$ , on the surface in a steady state which is maintained at high anodic current density ( $> 100\mu\text{A}/\text{cm}^2$  at  $-40$  degrees).

910. Clarke, T. G., Hampson, N. A., Lee, J. B. et. al.

46, 3437, (1968)

## Oxidations Involving Silver. I. Kinetics of the Anodic Oxidation of Silver in Alkaline Electrolytes.

The kinetics of the electrochemical oxidation of silver to  $\text{Ag}_2\text{O}$  in NaOH have been studied at different temperatures and hydroxyl ion concentrations. The enthalpy of activation was found to be  $\sim 5$  kcal/mole. The kinetics of oxidation of  $\text{Ag}_2\text{O}$  to AgO are discussed.



CANADIAN JOURNAL OF CHEMISTRY (Cont.)

906. Barradas, R. G., and Fraser, G. H.

42, 2488, (1964)

Kinetic Studies of the AgO/Ag<sub>2</sub>O Electrode in Alkaline Solutions.

The anodic oxidation of Ag<sub>2</sub>O to AgO in normal aqueous potassium hydroxide solution was investigated quantitatively under both galvanostatic and potentiostatic conditions at 25 degrees C. A few results for similar experiments in N/40 KOH are also reported. Tafel slopes and other parameters were determined. The experimental results show the dependence of current density as a hyperbolic function of overpotential, i.e.  $i = 2i_0 \sinh(\lambda F\eta/2RT)$ . The electron number  $\lambda$  was found to be 2 and the symmetry factor  $\beta$  was confirmed to be 1/2. It is proposed that the rate-determining step for the formation of AgO from Ag<sub>2</sub>O occurs at the Ag<sub>2</sub>O/AgO interface and involves the transfer of O<sup>2-</sup> ions.

907. Barradas, R. G., and Fraser, G. H.

43, 446, (1965)

Considerations of Absorbed Ionic Intermediates on the AgO/Ag<sub>2</sub>O Electrode in Aqueous Solution.

An experimental study of the kinetics for the electrochemical formation of AgO from Ag<sub>2</sub>O in aqueous alkaline solutions was reported in an earlier paper. The proposed mechanism for the rate-determining step was suggested to be the transfer of oxide ions across the mixed oxide interface. Further theoretical possibilities under Langmuir and Temkin conditions of surface coverages are considered here in the light of the previously obtained experimental data. In particular we examine the possibilities of the rate-determining step involving adsorbed ionic intermediates on the AgO/Ag<sub>2</sub>O electrode at the oxide/electrolyte interface. For the Temkin conditions, the intrinsic and induced heterogeneity models of Conway and his coworkers have been applied to our calculation of Tafel slopes. None of the mechanisms at the oxide/electrolyte interface were found to be rate-controlling.

908. Ryan, D. E., Dean, J. R., and Cassidy, R. M.

43, 999, (1965)

Cadmium Species in Basic Solution.

The principal cadmium-containing species in basic solutions varies with the concentration of hydroxide ion such that the solubility of cadmium hydroxide can be satisfactorily expressed, in solutions of high ionic strength, in terms of  $[\text{Cd}(\text{OH})^+] = 3.0 \times 10^{-9} [\text{OH}^-]^{-1}$ ,  $[\text{Cd}(\text{OH})_2]_{\text{soln}} = 1.0 \times 10^{-6}$ ,  $[\text{Cd}(\text{OH})_3^-] = 1.2 \times 10^{-6} [\text{OH}^-]$ , and  $[\text{Cd}(\text{OH})_4^{2-}] = 3.1 \times 10^{-6} [\text{OH}^-]^2$ . Since the solubility varies from  $10^{-4}$  to  $10^{-6}$  M, the predominant species at high concentrations of hydroxide ion is  $\text{Cd}(\text{OH})_4^{2-}$ ; at low concentrations of hydroxide ion  $\text{Cd}(\text{OH})^+$  is the principal cadmium-containing ion in solution. There is little free cadmium ion in solutions whose hydroxide ion concentration is greater than  $10^{-4}$  M.



CANADIAN JOURNAL OF TECHNOLOGY (Cont.)

1000. Casey, E. J., Bourgault, P. L., Lake, P. E.

34, 95, (1956)

Nickel Cadmium Batteries Part I. Sintered Plates From a New Canadian Nickel Powder.

Sintered plaques of high porosity and good mechanical strength have been made from a new domestic nickel powder. The plaques, when impregnated and given electrolytic oxidations and reductions in a test cell, gave electrical capacities at low rates of discharge equal to those of plates produced commercially from carbonyl nickel powder; and at extremely high rates gave 15–20% less than the commercial plates. Physical and electrical characteristics of the plates are interpreted in terms of the physical properties of the new powder and various factors in the processing. Certain problems which need detailed investigation are pointed out.

1001. Bourgault, P. L., Lake, P. E., Casey, E. J., Dubois, A. R.

34, 495, (1957)

Nickel-Cadmium Batteries II. Impregnation of Positive Plates  
By Thermal Decomposition of Aqueous Nickel Nitrate.

A method is described for placing electrochemically-active material in the pores of sintered nickel plaques. The plaque is first immersed in aqueous nickel nitrate; then the nickel nitrate in the pores is decomposed at high temperatures to an intermediate which converts rapidly to nickel hydroxide in caustic solutions. The effects of temperature and time of immersion and of thermal decomposition, and of the surrounding atmosphere, have been studied. Results on electrical behavior of the plates are presented, and a preliminary discussion of the mechanism of the impregnation process is offered.

## CHEMICAL PHYSICS, JOURNAL OF

1100. Rüetschi, P., and Delahay, P.

23, 556, (1955)

### Influence of Electrode Material on Oxygen Overvoltage: A Theoretical Analysis.

Variations of overvoltage for oxygen evolution from one metal to another primarily result from variations in the energy of the bond M—OH. The overvoltage decreases approximately in a linear manner with increasing bond energy. This relationship is verified experimentally for Ag, Au, Cd, Co, Cu, Fe, Ni, Pb, Pd, and Pt, for electrolysis in one' N potassium hydroxide at one amp  $\text{cm}^{-2}$ ; the experimental data are those reported by Hickling and Hill. Bond energies for M—OH are calculated by three different thermodynamic cycles involving, respectively, the standard heat contents of the hydroxide, the oxide, and spectroscopic data for molecules MO. Variations of the energy of the bond M—OH, as the electrode is oxidized to a higher valence, also account for sudden breaks in plots of overvoltage against logarithm of current density. Finally, there is essentially no correlation between the oxygen overvoltage for different metals and the corresponding work functions.

1101. Fordyce, J. S., and Baum, R. L.

43, 843, (1965)

### Vibrational Spectra of Solutions of Zinc Oxide in Potassium Hydroxide.

Raman and infrared reflection spectral studies of solutions of zinc oxide in potassium hydroxide (7.5 and 15m) with OH/ZnO ratios of from 8 to 16 show that the predominant species in these solutions possesses tetrahedral symmetry (Point Group  $T_d$ ) and is presumably the  $\text{Zn}(\text{OH})_4^{2-}$  ion. The frequencies and assignments, neglecting the hydrogen atoms, are:  $\nu_1(a_1) = 484 \text{ cm}^{-1}$ ,  $\nu_2(e) = 285 \text{ cm}^{-1}$ ,  $\nu_3(f_2) = 430 \text{ cm}^{-1}$ ,  $\nu_4(f_2) = 322 \text{ cm}^{-1}$ .

1102. Newman, G. H., and Blomgren, G. E.

43, 2744, (1965)

### NMR Study of Complex Ions in the Aqueous ZnO-KOH System.

Proton magnetic resonance measurements of the aqueous ZnO-KOH system have been made. Only a single resonance line is observed, but the position of the line depends on the concentrations of KOH and ZnO. Analysis of the data is consistent with the presence of only one zincate species. A value for the chemical shift of the zincate ion is derived, and also a more precise value for the chemical shift of KOH in water is determined. The significance of the results is discussed.



## CHEMICAL REVIEWS

1200. Nyholm, R. S.

53, 263, (1963)

### The Stereochemistry and Valence States of Nickel.

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CHEMICAL SOCIETY (LONDON), JOURNAL OF THE

1300. Wakkad, S. E. S., and Emara, S. H.

A, 3504, (1953)

The Anodic Oxidation of Metals at Very Low Current Density. Part II. Nickel.

The conflicting results of various workers on the variation of the anode potential with the quantity of electricity passed when the nickel electrode is forced from evolution of hydrogen to that of oxygen, as well as on the type of oxides formed on the surface of the metal before oxygen evolution, have been clarified by carrying out the anodic oxidation of nickel in solutions of different pH values at very low current density. It is shown that the oxides formed on the anode before evolution of oxygen depend on the polarising current; at extremely low current density the oxides NiO, Ni<sub>3</sub>O<sub>4</sub>, Ni<sub>2</sub>O<sub>3</sub>, and NiO<sub>2</sub> are formed before oxygen is evolved, but at higher current density only the oxides NiO, Ni<sub>2</sub>O<sub>3</sub>, and NiO<sub>2</sub> appear. The primary anodic products are however, the oxides NiO and NiO<sub>2</sub>, Ni<sub>3</sub>O<sub>4</sub> and Ni<sub>2</sub>O<sub>3</sub> being formed from a secondary reaction between NiO and NiO<sub>2</sub>. The higher oxides are unstable, decomposing to NiO, the most stable oxide in contact with the metal.

1301. Briggs, G. W. D.

348, 1846, (1957)

Structural Modifications of  $\beta$ -NiO-OH.

The existence of additional reflections in the X-ray diffraction pattern of  $\beta$ -NiO-OH is reported, and a modified form of the oxide obtained by electrodeposition in the presence of foreign ions is described.



CHEMIE-INGENIEUR-TECHNIK

1400. Harivel, J. P., Morignat, B., Migeon, J., Laurent, J. F.

6, 671, (1966)

**Investigation of the Physical-Chemical Mechanisms of the Oxide-Reduction of  
Porous Electrodes Impregnated with Cadmium Hydroxide.**

The influence of current intensity, temperature and KOH concentration in charging on the capacity of the electrodes is determined by measurement of the quantity of electricity given off in discharging with constant current density or constant voltage. These results, together with solubility determinations of the  $\text{Cd}(\text{OH})_2$  in KOH and X-ray fine structure analyses of the electrodes, permit conclusions concerning the physical-chemical processes on the negative plates of nickel/cadmium batteries.

1500. Labat, J.

60, 1253, (1963)

**On the Preparation and the Electrochemical Properties of Higher Nickel Oxides.**

The chemistry of higher nickel oxides and hydroxides and their behavior in alkaline solution have been the object of numerous, often contradictory researches; this account brings out the deep divergences still subsisting between the authors with regard to the formula and the properties of these oxides.



## CHEMISTRY IN CANADA

1600. Casey, E. J.

12, 49, (1960)

### Some Chemistry of the Nickel-Cadmium Battery.

This paper is intended to outline the results of some recent laboratory investigations which have resulted in a better understanding of the chemistry of this system, and to outline a few vexing problems which still await investigation.

## ELECTROANALYTICAL CHEMISTRY, JOURNAL OF

1700. Bauer, H. H.

12, 64, (1966)

### Electrochemical Behavior of Cadmium.

Studies of the electrochemistry of the Cd(II)/Cd(Hg) system by polarography have been characterized by two features:

(1) Frequently, "anomalous" behavior has been reported, *i.e.*, behavior indicating that the electrode process has a mechanism more complex than an electron-transfer step combined with solely diffusive mass transport.

(2) Results obtained in different investigations have not generally been in accordance. In ostensibly similar systems, anomalies have only sometimes been reported; even in the absence of anomalies, reported values for the kinetic parameters (rate constant  $k$ , transfer coefficient  $\alpha$ ) have generally differed.

It is proposed to show here that all reported observations are explicable by taking into account that mass transport is influenced by electrical migration of cadmium ions within the diffuse double layer.

1701. Breyer, B., Bauer, H. H.

12, 411, (1966)

### Electrochemical Cells as Electrical Circuit Elements.

The electrolytic capacitor is an example of the use, as a practical circuit element, of a sort of electrochemical cell in which no faradaic process occurs; for many years, these *electrolytics* have been the only practical capacitors of high capacity obtainable in a useful physical size at low cost.

It is the purpose of this discussion to bring under consideration the possible merits, as circuit elements, of electrochemical cells in which faradaic processes do, or can be made to, occur; such elements may logically and conveniently be referred to as *faradaics*.

1702. Kronenberg, M. L.

13, 120, (1967)

### Electrochemical Measurements of Thin Layers of Nickel Oxide.

In the work reported here the oxides were formed on 40-mil nickel wire (99.8% pure, Driver-Harris, Co., Harrison, New Jersey). The controlled electrochemical oxidation of a well defined surface at low current density permitted the formation of a reproducible, thin layer of the higher nickel oxide (approximately 1-2 molecular layers of oxide) avoiding a significant potential gradient within the oxide. A study of this electrochemically formed oxide also yielded important information regarding the nickel oxide-oxygen corrosion couple, oxygen evolution on nickel oxide and the electrochemical properties of the oxide films.



## ELECTROANALYTICAL CHEMISTRY, JOURNAL OF (Cont.)

1703. Farr, J. P. G., and Hampson, N. A.

13, 433, (1967)

### Evaluation of the Characteristics of Exchange Reactions.

#### 1. Exchange Reaction at a Solid Zinc Electrode in Alkali.

For the zinc exchange at solid zinc electrodes in alkali, a.c. impedance measurements have indicated that in the frequency range below 1 kc/sec the reaction is controlled by adatom diffusion. Furthermore, there is considerable evidence to suggest that intermediates are strongly adsorbed at the electrode interphase. Accordingly, it was decided to investigate the charge transfer reaction in the micro-second time range using the double impulse method whereby adatom diffusion effects would not interfere.

1704. Brown, D. S., Farr, J. P. G. et. al.

17, 421, (1968)

### The Differential Capacitance of Zinc in Aqueous Solution.

The kinetics of exchange of zinc in alkali have recently been investigated using both polycrystalline and single crystal (oooI) electrodes. The very high value obtained for the frequency-independent capacity ( $C_0$ ) shunting the double layer has been attributed in part to the adsorption of OH<sup>-</sup> on to the electrode surface.

Russian workers have independently reported differential capacitance curves for single crystal and polycrystalline surfaces of zinc in aqueous KCl (pH 7) and Na<sub>2</sub>SO<sub>4</sub> (pH 3) electrolytes; however, the Russian reports differ from each other in the values of the p.z.c. (point of zero charge) obtained from the capacitance minima, in the shapes of the curves, and in the extent of the observed regions of polarizability.

Previously, differential capacitance measurements on Ag and Cd in aqueous solution have been reported. The results of similar measurements on polycrystalline and single crystal (oooI) zinc surfaces are reported in the present paper.

1705. Conway, B. E., and Sattar, M. A.

19, 351, (1968)

### Electrochemistry of the Nickel Oxide Electrode.

#### Part VIII. Stoichiometry of Thin Film Oxide Layers.

Interest in thin film nickel oxide material studied in the present work arises in relation to: (a) stoichiometries and "active oxygen" content of thin layer materials; (b) constitution of thin layers in relation of self-passivation effects in anodic oxygen evolution (Part V<sup>14</sup>) and to passivation of the metal itself; (c) internal concentration polarisation effects which may arise with respect to the two or more states of oxidation of nickel (Ni(II), Ni(III), Ni(IV)) in *bulk* oxide material; hence, comparatively, the behaviour of thin film material may be of special interest; (d) possible avoidance of local isolation of reducible material on discharge, a situation that tends to occur in bulk impregnated plaques at high rates of discharge; (e) the ellipsometric results at nickel electrodes, studied by Bockris *et al.* and (f) the possible use of thin film cathode materials for pulsed charge and discharge conditions where high rate, short duration electrical fluxes are involved.

## ELECTROCHEMICAL SOCIETY, JOURNAL OF

1800. Hael, A. P.

76, 435, (1939)

### The Cadmium-Nickel Storage Battery.

The cadmium-nickel battery is widely used in Europe but not in America. It is particularly applicable to severe service conditions since the active material does not shed readily and wide temperature fluctuations have but little effect. The active material of the positive plates is nickel hydroxide plus pure crystalline graphite. In place of graphite metallic nickel flakes may be used. The active material of the negative plates is cadmium oxide or hydroxide. The effect of the presence of iron in the cadmium paste is discussed at length. Similarly the addition of lithium hydroxide to the KOH electrolyte is treated at length. On the basis of the author's experiments, the lithium appears superfluous in positive electrodes containing graphite except that it counteracts the deleterious effects of traces of iron. The adsorption of  $\text{CO}_2$  by the KOH electrolyte reduces the capacity of the battery, due to cadmium carbonate formation on the surface of the CdO grains. The new starting battery has very thin plates and very close spacing. It is replacing the lead storage battery in trucks and buses.

1801. Fleischer, A.

94, 289, (1948)

### Sintered Plates For Nickel-Cadmium Batteries.

Porous plaques are prepared by sintering carbonyl nickel powder of low apparent density. The plaques are impregnated with nickel or cadmium salt solutions and the heavy metal ions precipitated in the pores of the plaque by cathodic polarization in alkali hydroxide solution. Sintered plates made by this procedure have been assembled into experimental cells for study. A typical set of discharge curves is shown for a five plate experimental cell covering the range from the twenty hour rate to the three minute rate.

1802. Wagner, C.

99, 346c, (1952)

### The Electrochemistry of Ionic Crystals.

In recent years the electrical properties of solid halides, oxides, and sulfides have been widely investigated, particularly because these substances are used industrially in rectifiers and photocells, as phosphors, and for other purposes. In many cases, the electrical conductivity depends not only on temperature but also on small deviations from the ideal stoichiometric ratio of metal to nonmetal, the presence of foreign substances in small concentrations, and eventually on grain size and previous heat treatment. By and large, reproducible results can be obtained only if the significant chemical factors are adequately defined. Thus, the "electrochemistry" of ionic crystals has become an important topic of present research.

There are characteristic differences between the electrochemistry of aqueous solutions and the electrochemistry of ionic crystals, but still more remarkable seems the fact that there are basic problems which can be treated by analogy. This is especially true with systems involving predominant ionic conduction.



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

In the following, the analogies between problems of aqueous solutions and those of ionic crystals are stressed, in particular since the author has widely used such analogies in addition to concepts borrowed from physics and crystallography.

1803. Huber, K.

100, 376, (1953)

### Anodic Formation of Coatings on Magnesium, Zinc and Cadmium.

A report is given of recent investigations of anodically formed coatings on magnesium, zinc, and cadmium in NaOH and Na<sub>2</sub>CO<sub>3</sub> solutions. The growth of the coatings was followed by means of x-ray and electron diffraction and electron microscopy. It was found that the metal oxide was favored as initial product. Depending upon the relative magnitude of the solubility products, the coatings remained in the form of oxides or were converted into the respective hydroxides or carbonates. The semiconductance of the initial coatings was significant in determining the electrochemical behavior of the electrodes.

1804. Dirkse, T. P.

101, 328, (1954)

### The Nature of the Zinc Containing Ion in Strongly Alkaline Solutions.

The nature of the zinc-containing ion in strongly alkaline solutions was determined by measuring electrode potentials of zinc in such solutions under equilibrium conditions. Galvanic cells were used in which junction potentials were practically eliminated. Results indicate that in the concentration range of approximately 1–7M potassium hydroxide all the zinc is in the form of a zincate ion, Zn(OH)<sub>4</sub><sup>2-</sup>. The standard free energy of formation of this ion is –206.2 kcal.

1805. Dirkse, T. P.

102, 497, (1955)

### Electrolytic Oxidation of Zinc in Alkaline Solutions.

A study has been made of the mechanism of the reaction taking place when zinc is anodically treated in potassium hydroxide solutions. The zinc-containing ion present in solution as a result of the anodic treatment is Zn(OH)<sub>4</sub><sup>2-</sup>. However, zinc oxide or hydroxide is an intermediate leading to the formation of Zn(OH)<sub>4</sub><sup>2-</sup>. This latter ion then decomposes slowly to form zinc oxide.

1806. Work, G. W., Wales, C. P.

104, 67, (1957)

### Instrumentation for Use in Storage Battery Studies.

Instrumentation for use in a wide range of storage battery studies has been evolved. This storage battery analyzer features simplicity and accuracy of control, a wide scope of variables measured, and a complete, continuous record.

## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

A null-balance servo system controls the output of the rectified d-c power supply at any desired current or voltage by continuously regulating the a-c input. Individual plate potentials, temperature, gas concentrations, and gas volumes are continuously measured and recorded. Optional equipment permits additional types of automatic cycling or other use in varied applications. The possibilities of the use of such methods are briefly illustrated and discussed from data on some Ni-Cd cells.

1807. Hamer, W. J., Craig, D. N.

104, 206, (1957)

### A Reproducible and Stable Silver-Silver Oxide Electrode.

A method is described for the preparation of silver-silver oxide electrodes which are stable and reproducible. When used in cells of the type  $\text{Hg}(l), \text{HgO}(s) \mid \text{NaOH, aq.} \mid \text{Ag}_2\text{O}(s), \text{Ag}(s)$  the silver-silver oxide electrodes give stable potentials over periods of 38 days. No evidence was found that Ag,  $\text{Ag}_2\text{O}$  electrodes evolve oxygen, that  $\text{Ag}_2\text{O}$  exists in different forms in aqueous solutions at normal temperatures, that  $\text{Ag}_2\text{O}$  reverts to a lower oxide, or that imperfections exist in the  $\text{Ag}_2\text{O}$  crystal. The free energy and entropy changes for the reaction in the above cell are  $-11254$  cal. and  $-9.12$  e.u., respectively, at 25 degrees C. These values are reasonably consistent with the best available thermodynamic data. The standard electrode potential of the Ag,  $\text{Ag}_2\text{O}$  electrode is found to be  $-0.342$  v at 25 degrees C.

1808 Lake, P. E., Casey, E. J.

105, 52, (1958)

### The Anodic Oxidation of Cadmium 1. Mechanism of Film Formation.

Cadmium oxidizes anodically in hydroxide solutions to form films of reaction products which control the subsequent anodic processes. The electrometrics of film formation and reduction were determined, and various other definitive experiments were done which permit an interpretation of the general mechanism of oxidation to be made. The film forms as  $\text{CdO}$  which is converted into  $\text{Cd}(\text{OH})$ , at a rate dependent upon various experimental factors.

Interest in the Ni-Cd battery has focused our attention on the behavior of Cd during electrolytic oxidation and reduction in KOH electrolyte, both with and without  $\text{K}_2\text{CO}_3$  impurity.

The purpose of this work was to establish the nature of the anodic reactions on Cd metal in caustic electrolytes, and to try to determine the general mechanism of the process.

1809. Dirkse, T. P., DeHaan, F.

105, 311, (1958)

### Corrosion of the Zinc Electrode in the Silver-Zinc Alkali Cell.

A study has been made of the factors that affect or bring about the corrosion of the zinc electrode in a silver-zinc-alkali cell. Cells containing 30% potassium hydroxide as electrolyte were used and kept at room temperature. Special attention was centered on open circuit or stand conditions. This corrosion is affected primarily by oxygen and by dissolved silver oxides.



ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1810. Hadley, C. P., Rudy, W. G.

105, 395, (1958)

A Study of the Molded Nickel Cathode.

Research work on the molded nickel cathode is described. Results are given regarding the effects on emission and life on variations in nickel powder, alkaline-earth carbonates, reducing agents, sintering, and aging. Data on pulsed emission are presented.

1811. Graff, W. S., Stadelmaier, H.

105, 446, (1958)

Higher Oxides of Silver.

Samples of higher oxides of silver were prepared by several chemical and electrochemical procedures. Two distinct higher oxides were produced. The first, agentic oxide,  $\text{AgO}$ , is a black powder and has a monoclinic structure for which lattice constants are derived. There is no evidence of the existence of other crystalline forms of  $\text{AgO}$ . The second oxide, with silver in a valence state higher than plus two, is present in some preparations along with  $\text{AgO}$ . The stoichiometry was not determined. It is also black and has a face-centered cubic lattice. It decomposed to  $\text{AgO}$  gradually over a period of months.

1812. Dirkse, T. P., Werkema, G. J.

106, 88, (1959)

Electrolytic Transition of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$  in Alkaline Solutions.

An interrupted current technique was used to study the electrolytic oxidation of silver in alkaline solutions. The short voltage peak just preceding the stage corresponding to the production of  $\text{AgO}$  in the voltage-time curves is interpreted as being due to the high electrical resistance to the  $\text{Ag}_2\text{O}$  layer.

1813. Dirkse, T. P.

106, 154, (1959)

Composition and Properties of Saturated Solutions of  $\text{ZnO}$  in  $\text{KOH}$ .

In many alkaline batteries a soluble zinc anode is used. This produces, on discharge, a solution of  $\text{ZnO}$  or zincate in the electrolyte. To deal with such solutions theoretically, it is often necessary to know the values for certain physical properties of such solutions. For that reason saturated solutions of  $\text{ZnO}$  in  $\text{KOH}$  were prepared and studied at different temperatures.

1814. Croft, G. T.

106, 278, (1959)

Controlled Potential Reactions of Cadmium and Silver in Alkaline Solution.

Data are reported on the electrochemical oxidation and reduction of both cadmium and silver in potassium hydroxide electrolyte obtained using techniques in which the overpotential was the independent and the current the dependent variable. The rate of oxidation of cadmium is maximum at overpotentials of 18.0 and approximately 40.0 mv. The rate of reduction of cadmium and the rate of oxidation of silver are both monotonically increasing functions of the overpotential.

ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1815. Dirkse, T. P., Wiers, B.

106, 284, (1959)

The Stability and Solubility of AgO in Alkaline Solutions.

Silver oxide is stable in boiling water and decomposes but very little at room temperature in strongly alkaline solutions. The presence of  $\text{Ag}_2\text{O}$  does not affect this stability, but the presence of unoxidized silver does increase the rate of decomposition. When AgO dissolves in strongly alkaline solutions the dissolved form is primarily AgO and  $\text{Ag}(\text{OH})_3^-$ . The standard free energy of formation of the latter is  $-85,380$  cal/mole.

1816. Salkind, A. J., Zeek, W. C.

106, 366, (1959)

The Structure of AgO.

The structure of silver oxide (AgO) has been of interest to members of the Society as evidenced by recent articles in the Journal, and by discussions at the Ottawa Meeting.

We would like to draw the attention of readers of this Journal to a group of researchers whose earlier contributions to this field are often overlooked. We refer to the work of Vladimiro Scatturin and his associates at the University of Padua. Their most recent paper was entitled "The Crystalline Structure of AgO".

They investigated the crystal structure of AgO using both copper and iron radiation and listed in their paper 36 reflections obtained with Fe K $\alpha$  radiation. They were able to index all these reflections by the Ito method and concluded that the compound was monoclinic, Space Group  $C_2^6$   $h = C 2/C$  with the following parameters.

1817. Dirkse, T. P.

106, 453, (1959)

The Silver Oxide Electrode.

A review has been prepared of the electrochemistry of the silver oxide electrode. The discussion covers the structure and electrochemistry of the oxides of silver and their behavior in batteries.

1818. Lake, P. E., Casey, E. J.

106, 532, (1959)

The Anodic Oxidation of Cadmium 1. Mechanism of Film Formation.  
(Discussion of previous paper)

1819. Bank, J. F., Garrett, A. B.

106, 612, (1959)

A Study of the Silver (I) Oxide-Silver (II) Oxide Electrode.

A reproducible emf of the cell  $\text{Ag}(c), \text{Ag}_2\text{O}(c)/\text{NaOH}[(1M/\text{AgO}(c), \text{Ag}_2\text{O}(c))]$ , Pt is found to be 0.262 v at 25 degrees C. From this value and the known potential of the Ag,  $\text{Ag}_2\text{O}$  electrode, the standard oxidation potential of the  $\text{Ag}_2\text{O}$ , AgO electrode is  $-0.604$  v. The temperature coefficient of the cell is  $+2.20 \times 10^{-1}$  v/deg. The free energy, enthalpy, and entropy changes for the cell reaction are  $-6049$  cal,  $-4537$  cal, and  $5.07$  cal/deg, respectively. From these values and the existing thermodynamic data on Ag and  $\text{Ag}_2\text{O}$ , values of  $3463$  cal,  $-2769$  cal, and  $13.81$  cal/deg are calculated, respectively, for the free energy and enthalpy of formation and for the entropy of AgO at 25 degrees C.



ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1820. Palágyi, T. Z.

106, 846, (1959)

Investigations on the Silver-Zinc Alkaline Storage Battery by the Aid of Radioactive Isotopes.

The failure of silver-zinc storage batteries is generally caused by the negative electrode, and less often by the separator or the positive electrode. Both silver and zinc have isotopes with suitable hard gamma radiation and half-life of about  $\frac{3}{4}$  year; consequently these isotopes can be used easily for labelling of electrodes. This fact induced us to employ  $\text{Zn}^{65}$  and  $\text{Ag}^{110}$  isotopes for the purpose of life tests and for investigating processes taking place during storage of the cells.

Our method was based on the hypothesis that, if  $\text{Zn}^{65}$  isotope is deposited on one of the negative plates of the cell, then the path of the ions while cycling can be followed by the aid of the radioactive contamination of the surface of the nonlabelled plates. The same principle was used to label with  $\text{Ag}^{110}$  isotope the positive electrode of experimental cells and to follow the path of the dissolved silver ions.

1821. Wales, C. P., Burbank, J.

106, 885, (1959)

Oxides On The Silver Electrodes.

Silver electrodes were studied by means of potentials and x-ray diffraction patterns. The silver was charged anodically in 35% KOH by means of either constant current or constant potential, and discharged at a low or high rate. Attempts were made to form an oxide higher than AgO by means of anodization. The products of anodization of silver in 2N  $\text{H}_2\text{SO}_4$  were determined. The basis for the theory that the oxides of silver are formed by the introduction of oxygen into the octants of the face-centered cubic silver lattice was examined.

1822. Lake, P. E., Casey, E. J.

106, 913, (1959)

The Anodic Oxidation of Cadmium II. Electrical Properties of The Film.

Cadmium electrodes under anodic oxidation in hydroxide and carbonate electrolytes have been examined by analysis of the decay of overpotential after current interruption.

After passivation while oxygen is being evolved, except for a small instantaneous ( $< 1$  msec) ohmic drop, the potential decays logarithmically with time in the manner usually found for the decay of activation overpotential of a gas electrode. Before passivation while the metal is actively being oxidized, however, except for the small ohmic drop, the potential decays exponentially with time in two steps. This behavior is not described by activation theory.

Determinations were made of the capacitance of both the oxidizing and the passivated cadmium, both from potential decay curves and from superimposed a-c. All the a-c values correspond to those of a normal double layer, as to those obtained from decay measurements after



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

passivation has occurred. However, the values obtained from decay curves before passivation are two orders of magnitude higher early in the oxidation but drop rapidly toward the a-c values as oxidation proceeds.

It is proposed that next to the Helmholtz double-layer at the CdO-electrolyte interface, there exists a highly polarized inner double-layer in which the reaction  $\text{OH}^- \rightarrow \text{O}^- + \text{H}^+$  takes place. When the field strength across the inner double layer becomes high enough for the reaction  $\text{OH}^- \rightarrow \text{OH} + \text{e}^-$  to take place instead, oxygen is evolved and the electrode passivates.

The roles of adsorption of  $\text{OH}^-$  to form the Helmholtz layer and of interference by  $\text{CO}_3^{2-}$  are discussed in terms of the results.

1823. Dirkse, T. P.

106, 920, (1959)

### The Oxidation of the Silver Electrode in Alkaline Solutions.

The formation of  $\text{Ag}_2\text{O}$  and  $\text{AgO}$  was studied by means of constant current and constant potential processes. The efficiency of these oxide formations was determined by measuring the gain in weight of Ag electrodes under various conditions of charge, and the extent of the polarization of these processes was measured by using an interrupted current technique.

1824. Dirkse, T. P., Vrieland, E. G.

106, 997, (1959)

### A Study of Zinc Noble Metal Couple in Alkaline Solutions.

A metal-like coating is formed frequently on copper or silver leads which are attached to the zinc electrodes in commercial zinc-alkaline cells. This coating is zinc or a zinc-rich alloy. The conditions under which this coating is formed have been studied, and several possible mechanisms for its formation are presented and discussed.

1825. Kordesch, K., and Marko, A.

107, 480, (1960)

### Sine Wave Pulse Current Tester for Batteries

An instrument has been developed which measures the voltage of a battery during discharge, eliminating its ohmic component. The instrument is portable operated on 60 cycle alternating current and features direct meter readings (instead of an oscilloscope). Its simplicity and ruggedness make it especially suited for development and production control tasks. Results of measurements on different types of cells are presented to illustrate the wide applicability of the instrument.

1826. Croft, G. T.

107, 571, (1960)

### Controlled Potential Reactions of Cadmium and Silver in Alkaline Solutions. (Discussion of a previous paper)

## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1827. Falk, S. U.

107, 661, (1960)

### Investigations on the Reaction Mechanism of the Nickel Cadmium Cell.

X-ray diffraction patterns from electrodes submerged in electrolyte have been obtained during charge and discharge by means of a special test cell, and the composition of the active materials has been determined. The question whether  $\text{CdO}$  or  $\text{Cd(OH)}_2$  is formed during discharge has been subject to special attention. The low potential reaction of the positive plate has been studied. The emf and the  $dE/dT$  have been determined between  $-40$  degrees and  $+50$  degrees C at various states of charge

1828. Cahan, B. D., Ockerman, J. B., Amlie, R. F.

107, 725, (1960)

### The Silver-Silver Oxide Electrode.

An a-c square wave technique was used to study resistance and double-layer capacity during film formation on silver electrodes in KOH solutions. The peak in the voltage-time curve at constant current anodization is shown to coincide with complete surface coverage by  $\text{Ag}_2\text{O}$  and is not an ohmic resistance, but rather an overvoltage effect. Evidence for the existence of an unstable higher oxide than  $\text{AgO}$  (or additional oxygen) during oxygen evolution is presented. Microvolumetric gas measurements with large area electrodes on open-circuit decay also support this conclusion. The duration of the upper voltage plateau of the voltage-time curve during discharge of  $\text{AgO}$  electrodes is determined by contact phenomena among individual  $\text{AgO}$  particles, in particular by separation and passivation of the remaining  $\text{AgO}$  by insulating surface layers of  $\text{Ag}_2\text{O}$ .

1829. Dirkse, T. P.

107, 859, (1960)

### The Cathodic Behavior of $\text{AgO}$ in Alkaline Solutions.

A study has been made of the discharge of  $\text{AgO}$  to determine why only a part of the discharge capacity of  $\text{AgO}$  is delivered at the potential of the  $\text{AgO-Ag}_2\text{O}$  couple and to determine the role of oxygen in this process. The difference in discharge capacity of electrodes produced by constant-current and by constant-potential anodization also has been studied. A mechanism involving the transport of  $\text{O}^-$  ions through the electrode material and the reaction of these ions with the electrolyte is presented.

1830. Palágyi, T. Z.

108, 201, (1961)

### Investigation on the Silver-Zinc Storage Battery With Radioactive $\text{Zn}^{65}$ Isotope.

$\text{Zn}^{65}$  isotope was deposited electrolytically on the middle negative electrode of silver-zinc storage batteries assembled in three different ways. The path of the dissolved zinc ions



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

could be followed by measuring the radioactivity of the nonlabelled electrodes. In the deteriorated cells all the negative and nearly all the positive plates became contaminated with the isotope. The cycle life was longest with cells assembled tightly and with little electrolyte.

1831. Wales, C. P.

108, 395, (1961)

### The Silver-Silver Oxide Electrode 1. Anodic Oxidation in Alkaline Solutions.

Silver electrodes were oxidized anodically at 25 degrees C in 35 or 50% KOH at constant charge currents that ranged from the  $\frac{1}{2}$  to 40 hr rates. The electrodes were given both partial and complete charges. Except at a low charging rate the capacity was higher in 35% KOH than at 50% KOH. Oxidation was highly efficient at the first two potential plateaus. During a charge at the  $\text{Ag}_2\text{O}/\text{AgO}$  plateau initially  $\text{Ag}_2\text{O}$  oxidizes to  $\text{AgO}$  and then the prevailing reaction is  $\text{Ag}$  oxidizing to  $\text{AgO}$ . Simultaneously some  $\text{AgO}$  reacts with  $\text{Ag}$  to give  $\text{Ag}_2\text{O}$ . Under certain discharge conditions  $\text{AgO}$  may reduce directly to  $\text{Ag}$ , with  $\text{Ag}_2\text{O}$  forming as a secondary product.

1832. Duddy, J. C., Salkind, A. J.

108, 717, (1961)

### High Energy; Weight Ratio; Nickel Cadmium Cells.

Conventional nickel cadmium cells contain the active materials in either porous sintered nickel plaques or in nickel or nickel-plated steel pockets or tubes. A new process, adaptable to continuous methods of production, has been developed in which the active and conductive materials are dispersed in a microporous plastic structure. Cells with the high energy to weight ratio of 40 whr/kg have been constructed. Cell volumes are equal to those of the sintered plate design for equivalent capacities.

1833. Hills, S.

108, 810, (1961)

### Thermal Coefficients of EMF of the Silver (I) and the Silver (II) Oxide-Zinc-45% Potassium Hydroxide Systems.

Recently increased research efforts on the silver oxide-zinc couple reflect the increasing importance of this system. Some thermodynamic data for this system have already been reported but the reproducibility was too poor to indicate adequate reliability. This note presents additional electrochemical data and thermodynamic values derived therefrom.

This was true also for the deviations between the two monovalent silver oxide cells, indicating that the electrodes had come to equilibrium. However, the two divalent silver oxide cells continuously differed by approximately 1 mv.

ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1834. Amlie, R. F., Rüetschi, P.

108, 813, (1961)

**Solubility and Stability of Silver Oxides in Alkaline Electrolytes.**

The solubility of  $\text{Ag}_2\text{O}$  and  $\text{AgO}$  in alkaline electrolytes has been studied with a polarographic technique, using a rotating platinum electrode. Only a monovalent (and no divalent) silver species could be detected in solutions which had been in intimate contact with  $\text{AgO}$  powder over prolonged periods of time.

Quantitative measurements of the solubility of  $\text{Ag}_2\text{O}$  in  $\text{KOH}$  solutions ranging from 1-14 moles per liter, were carried out utilizing a potentiometric titration method. The solubility has a maximum at about 6N  $\text{KOH}$  where it reaches a value of  $4.8 \cdot 10^{-4}$  N.

The rate of the decomposition reaction  $2\text{AgO} \rightarrow \text{Ag}_2\text{O} + \frac{1}{2}\text{O}_2$  in alkaline electrolytes was investigated with a very sensitive microvolumetric method. The reaction rate increases with increasing hydroxyl ion concentration and is sensitive to daylight. The decomposition appears to proceed at the solid-liquid interface. Any divalent silver dissolving in minute amounts into the electrolyte is decomposed rapidly due to its instability. The decomposition proceeds at a rate of about 16% in 1 year at 30 degrees C and 49% in 1 year at 45 degrees C. This reaction can contribute significantly to the self-discharge of  $\text{AgO-Zn}$  batteries.

1835. Scatturin, V., Bellon, P. L.

108, 819, (1961)

**The Structure of Silver-Oxide Determined by Means of Neutron Diffraction.**

The crystal structure of  $\text{AgO}$  has been determined by means of neutron diffraction. The nuclear scattering of Ag and O atoms has made it possible to determine the positions of the oxygen atoms and to modify the space group which was reported for this compound from x-ray data. No magnetic diffractions were observed even at liquid helium temperature; the absence of magnetic scattering confirms the diamagnetism of the compound. The lattice was found to be monoclinic, space group  $P 2_1/c$ , with four formula weights of  $\text{AgO}$  in the unit cell. The silver atoms are not equivalent, and in the structure there are two Ag-O distances of 2.18 Å and 2.03 Å; the first one corresponds to colinear  $\text{Ag(I)-O}$  bonds, the second distance corresponds to square planar  $\text{Ag(III)-O}$  bonds.

1836. Palágyi, T. Z.

108, 904, (1961)

**Investigation on the Silver Zinc Storage Battery With Radioactive  $\text{Ag}^{110}$  Isotope.**

The results of experiments carried out with  $\text{Zn}^{65}$  isotope on the silver-zinc storage batteries were presented before. Here the results of investigations performed with  $\text{Ag}^{110}$  isotope are described.



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1837. Eisenberg, M., Bauman, H. F., Brettner, D. M.

108, 909, (1961)

### Gravity Field Effects on Zinc Anode Discharge Alkaline Media.

Under conditions of zero-gravity such as may prevail in satellites and space vehicles the absence of free convection may represent a major problem in the use of some primary or secondary batteries. An experimental study was carried out on smooth zinc anodes in 30% KOH solutions in which constant current discharge at various current densities was carried out to the point of passivation. By use of three different orientations in the gravitational field, different modes of mass transfer were obtained. An extrapolation of the results for low current density and long duration runs (over 20 sec) led to three limiting current densities values for the three positions. These values were also calculated from theoretical equations using measured or estimated physical properties. The importance of free convection vs. diffusion was also demonstrated by means of incremental fixed current-time experiments which determined anode capacity to passivation. Physical properties of the system were measured and anodic dissolution studies were made to obtain the necessary data for calculations. The gravity field effects important in systems involving density gradients would become even more important under the influence of larger accelerations in space vehicles or missiles. These accelerations could produce sizable differences in the performance of porous zinc anodes.

1838. Dirkse, T. P.

109, 173, (1962)

### The AgO—Ag<sub>2</sub>O Electrode in Alkaline Solution.

The standard potential of the AgO/Ag<sub>2</sub>O/OH<sup>-</sup> electrode has been found by direct measurement against a hydrogen electrode to be  $0.599 \pm 0.001$  v at 25°C. The value appears to vary slightly with KOH concentration. Furthermore, dE/dT values appear to change with KOH concentration as well as with temperature. Voltages measured with pellets of AgO and Ag<sub>2</sub>O show that the voltage is determined by the materials present at the grid.

1839. Salkind, A. J., Bruins, P. F.

109, 356, (1962)

### Nickel Cadmium Cells 1. Thermodynamics and X-Ray Studies.

Voltage decays of electrodes in sintered type nickel-cadmium cells were measured in cells stored at temperatures between -18 degrees and 52 degrees C. The heat of reaction of the cell was calculated to be -64 kcal/g mole. The solid reaction products of the cell were studied, *in situ*, by x-ray techniques, in special cells designed to fit on an x-ray diffractometer.

1840. Salkind, A. J., Duddy, J. C.

109, 360, (1962)

### The Thermal Runaway Condition in Nickel Cadmium Cells and Performance Characteristics of Sealed Light Weight Cells.

The thermal runaway condition, sometimes called the vicious cycle, can be caused in almost any type of cell under certain conditions. The underlying causes of the runaway con-

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dition are discussed with specific application to sealed nickel-cadmium cells on constant potential overcharge. The discharge and overcharge performance characteristics of sealed nickel-cadmium cells with plastic electrodes are presented. These cells operated at high energy density levels on both a weight and volume basis and were more difficult to put in the runaway condition.

1841. Eicke, Jr., W. G.

109, 364, (1962)

### The "Vicious Cycle" in Secondary Batteries—A Mathematical Approach.

Equations relating voltage, temperature, heat capacity, time, and current have been derived for a cell on constant-potential charge. Assuming the cell to be fully charged and thermally isolated from its surroundings, thereby retaining all of the electrical energy supplied to it, the equations derived are

$$1/i = \frac{1}{i_o} - \left( \frac{(V_a - V_{\Delta H}) (\Delta H^* - aF\eta)}{2RT_o^2 C_p} \right) t$$

and

$$1/T = \frac{1}{T_o} + \left( \frac{2R}{\Delta H^* - aF\eta} \left[ \ln \frac{i_o}{i} \right] \right) t$$

where  $i$  is the current,  $t$  the time,  $T$  the absolute temperature,  $V_a$  the applied voltage,  $V_{\Delta H}$  the voltage corresponding to the fraction of the electrical energy converted into chemical energy,  $\Delta H^*$  the activation energy for the electrode reaction,  $a$  the transfer coefficient,  $\eta$  the activation overpotential,  $i_o$  and  $T_o$  the initial current and temperature, respectively, and  $C_p$  the heat capacity of the cell. The equations have been verified experimentally. The case where cooling occurs is also considered.

1842. Makrides, A. C.

109, 977, (1962)

### Hydrogen Overpotential on Nickel in Alkaline Solution.

The exchange current, Tafel slope, stoichiometric number, and limiting anodic current of the hydrogen reaction on nickel on 0.1N NaOH depend on the pretreatment and the polarization history of the electrodes. The discharge step of the Volmer-Tafel mechanism is rate-determining on surfaces characterized by high fractional coverage with adsorbed hydrogen. Such surface states are metastable however and are transformed on anodic-cathodic cycling to states which adsorb hydrogen weakly. The exchange currents for the discharge and combination steps are then about equal.



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1843. Hampson, N. A., Tarbox, M. J.

110, 95, (1963)

The Anodic Behavior of Zinc in Potassium Hydroxide Solution I. Horizontal Anodes.

A study of the anodic behavior of horizontal zinc electrodes in KOH solution has shown that the equation

$$(i - i_1) t^{1/2} = k$$

holds for concentrations in the range 1-13.8M and passivation times in the range 10-800 sec. The constant  $k$  depends on the KOH concentrations and attains a maximum value in the region of 8.5M KOH;  $i_1$ , the maximum current density attainable without passivation, from a least squares fit is very near zero in all cases. From the linear parts of the curves connecting anode potential and time, value of  $dE/dT$  indicate that the conductivity of the anodic product prior to passivation depends on the concentration of the KOH electrolyte. This conductivity passes through a maximum in the same region as that which produces the longest passivation times.

1844. Weininger, J. L., Breiter, M. W.

110, 484, (1963)

Effect of Crystal Structure on The Anodic Oxidation of Nickel.

The formation of  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  on different crystal planes of nickel, and of polycrystalline nickel, was studied in alkaline solution. Oxide films of less than two monolayers were reduced potentiostatically, then current-potential curves were measured in the range -200 to 1600 mv at different rates of the linearly increasing potential. Electron diffraction and microscopy were used to develop a suitable experimental procedure for dealing with bare and smooth nickel surfaces. The extent of oxide film formation in air on different planes was in the order  $(110) > (100) > (111)$ . The reactivity on anodization, characterized by the potential at which the equivalent of one monolayer of hydroxide is formed, was in the same order: On continued oxidation the structure of the crystal surface is lost; subsequent reduction forms a strongly disordered surface. The results are discussed with regard to the mechanism of anodization, the extent of differences between crystal planes, and the conditions under which they are maintained or lost.

1845. Fleischmann, M., Thirsk, H. R.

110, 688, (1963)

The Growth of Thin Passivating Layers on Metallic Surfaces.

The main problem in interpreting the passivation of metals in terms of a theoretical model lies in the nature of the "passivating material." Discussion repeatedly returns to this

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question, and the answer usually takes one of two extreme forms, the first: passivation is due to a three-dimensional film of a definite chemical phase; the second: passivation is due to a disordered monomolecular array of absorbed ions or molecules. In the light of the discussion given in this paper we might well add a third form: passivation is due to an ordered monomolecular, two-dimensional film of a definite chemical phase.

1846. Horne, R. A., Bannon, W. J., Sullivan, E., Frysinger, G. 110, 1282, (1963)

### The Effect of Pressure on the Conductivity of Battery Electrolytes.

The electrical conductances of battery electrolytes have been measured at one atmosphere and of relatively dilute solutions of other electrolytes at elevated pressures, but inadequate information exists concerning the effect of pressure on the electrical conductance of battery electrolytes such as concentrated KOH and  $\text{H}_2\text{SO}_4$  solutions.

1847. Wales, C. P. 111, 131, (1964)

### Charging the Silver Oxide Electrode with Periodically Varying Current I. Brief Increases of Current.

Pulses of charge current were added to a constant charge current while a silver electrode was being charged (anodically oxidized) at the 20-hr rate. While charging at the  $\text{Ag}_2\text{O}/\text{AgO}$  potential plateau the polarization was lower following a pulse than it was before the pulse. This is believed to be the result of breaking the oxide layer. In 35% KOH the discharge capacity following a charge with pulses reached a maximum that could be considerably greater than the normal capacity. Capacity then decreased as the charge pulse current, pulse length, or pulse frequency increased. In 50% KOH the capacity was always below normal after similar pulses. A commercial silver-zinc secondary cell containing 44% KOH gave intermediate results.

1848. Dirkse, T. P., Vanderlugt, L. A. 111, 629, (1964)

### Factors Affecting the Transport of Ag in Ag-Alkaline Batteries.

A study has been made of the factors which control the amount of silver which is introduced into the electrolyte during the operation of a silver-alkaline battery. Part of this work was done with the use of radioactive silver as a tracer. Silver is introduced into the electrolyte during all phases of the operation of a silver-alkaline battery. However, it can be increased by charging at lower current densities or by operation at the  $\text{Ag}/\text{Ag}_2\text{O}$  voltage level. A possible mechanism for the electrolytic formation of the oxides is also given.



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1849. Weininger, J. L., Breiter, M. W.

111, 707, (1964)

Hydrogen Evolution and Surface Oxidation of Nickel Electrodes in Alkaline Solution.

The electrochemical processes which occur on nickel electrodes in 4N KOH during a slow-speed anodic potential sweep between  $-300$  and  $+1500$  mv were studied. Tafel plots for hydrogen evolution were determined under different conditions, and the impedance was measured at 100 cps as a function of potential. The results are interpreted in terms of the adsorbed species. It is confirmed that hydrogen evolution between  $-300$  and  $-100$  mv is controlled by the discharge step of water molecules (Volmer reaction) and that the coverage with electrochemically active hydrogen atoms is small in this region. Prior to the formation of  $\text{Ni(OH)}_2$ , an adsorbed layer of OH-radicals appears to be formed.

1850. Burbank, J., Wales, C. P.

111, 1002, (1964)

Electrolytic Cell for X-Ray Diffraction Studies of Electrode Phenomena.

This report describes a cell designed for use on a General Electric horizontal circle x-ray spectrogoniometer, permitting the x-ray examination to be made simultaneously with electrochemical measurements and visual observations.

1851. Posey, F. A.

111, 1173, (1964)

Methods for the Calculations of Polarization in Porous Electrodes.

Solutions in closed form are presented for the polarization behavior and the distribution of current and potential in idealized, one-dimensional porous electrodes in the case of a simple oxidation-reduction reaction under pure activation control. Exact solutions are derived for transfer coefficients of  $1/3$ ,  $1/2$ , and  $2/3$  for electrodes of finite length, while solutions for semi-infinite electrodes are given for transfer coefficients of  $1/4$ ,  $1/3$ ,  $1/2$ ,  $2/3$ , and  $3/4$ . An approximate method for calculating current and potential distributions in porous electrodes is proposed which is valid for any value of the transfer coefficient, and exact and approximate solutions are compared.

1852. Tuomi, D.

112, 1, (1965)

The Forming Process in Nickel Positive Electrodes.

A detailed study has been made of the phases produced and their geometric distribution during formation of Edison-type tubular positive nickel electrodes. The initial charging in lithiated KOH electrolytes, converts the  $\text{Ni(OH)}_2$  to a beta phase having a solid solution range for di- and tetravalent nickel. The beta crystalline structure is related to  $\text{LiNiO}_2$ . This phase

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can be further oxidized to alpha phase, a tetravalent nickelate having appreciable trivalent nickel solid solubility. Alpha phase is most readily formed during  $\text{Ni(OH)}_2$  oxidation in concentrated KOH or NaOH electrolytes, but does not form in LiOH electrolytes. The addition of LiOH to the battery electrolyte contributes to alpha phase discharge and limits alpha phase reformation. The contribution of alpha phase to electrochemical capacity is limited by a low effective exchange current as compared to the beta phase.

1853. Wales, C. P., Burbank, J.

112, 13, (1965)

### Oxides on the Silver Electrode II. X-Ray Diffraction Studies of Working Silver Electrodes.

Silver electrodes were examined in 20-50% KOH using a cell permitting simultaneous x-ray diffraction and electrochemical studies. Highly oriented smooth rolled sheet Ag developed randomly oriented Ag on its surface during early cycles. Charge-discharge capacity increased to a maximum as surface area increased. AgO crystal size and amount formed varied inversely with charging c.d. High charge rates gave tight coatings of small AgO crystals that ignited further oxidation. Reactions took place initially at the outer surface of the electrode. Oxidation to  $\text{Ag}_2\text{O}$  and AgO and reduction to  $\text{Ag}_2\text{O}$  and Ag occurred by formation of distinct crystals rather than expansion or contraction of preexisting crystal lattices. Discharge capacity at the AgO/ $\text{Ag}_2\text{O}$  potential plateau depended more on surface area than on quantity of AgO. A slow discharge produced smoother Ag surfaces, lowering capacity of the next cycle. There was never evidence of a suboxide, oxidation state higher than AgO, solid solution, or alloy of oxygen and silver.

1854. Shepherd, C. M.

112, 252, (1965)

### Design of Primary and Secondary Cells I. Effect of Polarization and Resistance on Cell Characteristics.

The current density distribution in a battery is a function of electrode height, electrode resistance, electrolyte resistance, and polarization. Mathematical solutions have been obtained for those cases where the polarization curves are either linear, logarithmic, or cubic. A numerical method is indicated for finding a general solution. In the case of linear polarization, the results are presented in graphs which show the current density distribution and other cell characteristics over a wide range of operating conditions. The determination of these cell characteristics can be of considerable importance in cell design. For practical applications, the complex mathematical calculations involved in the cases of logarithmic and cubic polarization can be eliminated by the use of transformations which convert them to the linear case.



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1855. Casey, E. J., DuBois, A. R., Lake, P. E., Moroz, W. J.

112, 371, (1965)

### Effects of Foreign Ions on Nickel Hydroxide and Cadmium Electrodes.

The behavior of individual positive and negative electrodes of the sintered-plate nickel-cadmium battery system in the presence of foreign ions in KOH solutions has been examined. Carbonate choke: The variation of electrochemical capacity as a function of carbonate contamination of the electrolyte, temperature, and current density was measured for both positive and negative electrodes. The effect of carbonate on the negative cadmium electrode is much greater than on the positive. The general mechanism and the role of intermediate complexes are discussed. Nitrate shuttle: Self-discharge occurs in cells containing nitrate, as a result of reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  at the cadmium electrode with subsequent reoxidation to  $\text{NO}_3^-$  at the nickel hydroxide electrode. Cations on the positive: Addition of  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{Sb}^{+3}$ ,  $\text{Al}^{+3}$ , and  $\text{As}^{+3}$  to the electrolyte had effects on capacity and on charge-retention of well-formed nickel hydroxide positive electrodes. Lithium promoted the highest average oxidation, particularly at high temperatures (55 degrees C). Arsenic was the best inhibitor of loss of charge. Possible mechanisms are discussed.

1856. Gubbins, K. E., Walker, Jr., R. D.

112, 469, (1965)

### The Solubility and Diffusivity of Oxygen in Electrolytic Solutions.

Measurements of the solubility of oxygen in sulfuric acid, phosphoric acid, and potassium hydroxide are reported, together with values of the diffusivity of oxygen in potassium hydroxide solutions at 25 degrees C. It is shown that for the electrolyte concentrations commonly employed in fuel cells the solubility and diffusivity of oxygen may each be reduced to as little as 2% of their corresponding values for pure water.

1857. Shepherd, C. M.

112, 657, (1965)

### Design of Primary and Secondary Cells II. An Equation Describing Battery Discharge.

A discussion is given of the derivation and application of an equation which gives an excellent description of a wide variety of cell and battery discharges. This equation gives the cell potential during discharge as a function of discharge time, current density, and certain other factors. It makes possible a complete description of cell discharge characteristics, using a minimum of experimental data and at the same time pinpointing experimental errors. It can also be used to describe cell charges, capacities, power evolution, and to predict capacities. A description is given of a simple numerical method for fitting this equation to a particular set of battery discharge curves. A graphical method is described for comparing characteristics of various types of cells.

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1858. Kober, F. P.

112, 1064, (1965)

### Analysis of the Charge-Discharge Characteristics of Nickel Oxide Electrodes by Infrared Spectroscopy.

Infrared spectroscopy is shown to be a sensitive tool in studies of the structure of electrochemically active materials and in elucidating the mechanism of charge and discharge. The spectrum of the sintered nickel-oxide electrode, impregnated using standard procedures, has been determined in the region between 4000 and  $250\text{ cm}^{-1}$ . These spectral data shown the discharged state to be  $\text{Ni}(\text{OH})_2$  having a hexagonal layer structure isomorphic with the space group  $D_{3d}^3$ . The hydroxyl groups are parallel to the c-axis of the crystal and are "free" in the sense that hydrogen bonding is absent. Associated with this structure is a relatively small amount of water which is trapped in the crystal lattice through the formation of coordinate-covalent bonds with the nickel ions. The charging process is accompanied by the formation of a hydrogen-bonded structure possessing a higher degree of crystal symmetry than is found in the discharged state. During discharge, these hydrogen bonds are continuously broken, and the structure transforms back to a free hydroxyl configuration.

1859. Jost, E., Rufenacht, F.

113, 97, (1966)

### Polarization Studies on Sintered Plate Electrodes Containing Various Amounts of $\text{Ni}(\text{OH})_2$ .

Porous, sintered plate, nickel oxide electrodes containing varied amounts of active material (nickel hydroxide) were investigated with a single pulse interruption technique. Double layer capacitance measurements and long time overvoltage decay suggest that the nickel hydroxide deposited in the pores in sequential impregnations is deposited as a sponge of discrete particles. The available surface area proves, therefore, to be proportional to the  $\text{Ni}(\text{OH})_2$  weight. The long decay times indicate solid-state diffusion or relaxation phenomena on top of liquid concentration overvoltage, which becomes increasingly important with heavily impregnated electrodes.

1860. Kober, F. P., Lublin, P.

113, 396, (1966)

### Potassium Distribution in Nickel-Oxide Electrodes.

Various authors have considered the role and distribution of potassium ion in the electrochemical oxidation of nickel-oxide electrodes in alkaline solution. Bourgault and Conway were able to relate extrapolated values of the "reversible" electrode potential to the activity of  $\text{H}_2\text{O}$  and  $\text{KOH}$  in the electrochemical oxidation reactions using the data of Akerlof and Bender. Their results indicate the association of hydrated  $\text{KOH}$  with the charged state. A formal reaction is given and shows the discharged state to be free of any adsorbed  $\text{KOH}$ . These results are in qualitative agreement with the previous work of Kornfeil. Neither of these authors has considered the inclusion of potassium into the crystal structure of the active materials.



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1861. Bro, P., Cogley, D.

113, 521, (1966)

A Stable High-Valency Nickel Oxide.

A high-valency amorphous nickel oxide prepared by the hypochlorite oxidation of nickel nitrate exhibited a mixture of oxidation states characterized by a mean nickel valency of approximately 3.5. The high-valency amorphous oxide was stable in strongly alkaline solutions, but it decomposed rapidly below pH 9. The oxide discharged efficiently when used as a cathode in an alkaline primary cell.

1862. Breiter, M. W., Weininger, J. L.

113, 651, (1966)

Anodic Oxidation of Cadmium and Reduction of Cadmium Hydroxide  
and Oxide in Alkaline Solutions.

The anodic oxidation of smooth cadmium and the subsequent reduction of cadmium hydroxide and oxide were studied by voltammetric methods with and without superimposed a-c voltage. Under voltammetric conditions a layer of  $\text{Cd}(\text{OH})_2$  appears to be formed at potentials below the passivation potential. Passivation results from a continuous thin film which forms at potentials between 0.005 and 0.1v. The small capacitance and the large resistance of the interface electrode/solution are due to this film. On reduction the thin film is reduced first. A pseudocapacitance which is attributed to the adsorption of OH radicals is observed during the anodic sweep in a potential range where formation of  $\text{Cd}(\text{OH})_2$  or  $\text{CdO}$  is not yet possible.

1863. Wales, C. P.

113, 757, (1966)

Charging the Silver Oxide Electrode with Periodically Varying Current II.  
Repeated Open Circuit Periods.

Sintered silver electrodes were oxidized anodically in 35-50% KOH at 25 degrees C, usually at the 20-hr rate, sometimes at faster rates. Length of charge plus open-circuit periods varied from 8 hr to 1/60 sec. A particular charge length and open-circuit length was repeated until oxygen evolution occurred. In 50 or 45% KOH this charge method gave either the same capacity as a constant d-c charge or less capacity, but in 35% KOH the improvements averaged as high as 40% under certain conditions. Best results were obtained when the preceding discharges were at low rates.

1864. Aia, M. A.

113, 1045, (1966)

Hydrothermal Studies of the System  $\text{NiO} - \text{H}_2\text{O}$ .

Crystal growth and phase changes in the system  $\text{NiO} - \text{H}_2\text{O}$  were studied by treating precipitated  $\text{Ni}(\text{OH})_2$  in a hydrothermal apparatus at temperatures from 200 degrees to 400 de-



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degrees C and  $\text{H}_2\text{O}$  pressures from 0.2 to 2.1 kbar (kilobars). The only solid phases found were  $\text{Ni}(\text{OH})_2$  with the brucite structure and  $\text{NiO}$  with the rocksalt structure. At  $285 \text{ degrees C} \pm 5$  degrees C  $\text{Ni}(\text{OH})_2$  converted to  $\text{NiO}$ , with very little effect of pressure on decomposition temperature. The best crystals of  $\text{Ni}(\text{OH})_2$  were obtained by treatment of 40% KOH solution at 200 degrees C and 1.0 kbar. It was not possible to convert  $\text{NiO}$  to  $\text{Ni}(\text{OH})_2$ . Hydrothermal treatment of  $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which was poorly crystallized, gave a black material exhibiting a novel x-ray diffraction pattern containing the lines of  $\gamma\text{-NiOOH}$ .

1865. Makrides, A. C.

113, 1158, (1966)

### Electrochemistry of Surface Oxides.

The electrochemical properties of surface oxides, particularly as they affect redox reactions at electrodes, are discussed. Experimental results on the effects of surface oxides on hydrogen evolution on nickel, on redox reactions on iron, on the hydrogen peroxide reactions on gold, and on oxygen evolution on lead are presented and discussed. The kinetics of formation and reduction of surface oxides are also examined with particular reference to gold electrodes where extensive measurements have been obtained.

1866. Shepherd, C. M., Langelan, H. C.

114, 8, (1967)

### High Rate Battery Electrodes.

It has been shown previously that metal plates of controlled porosities and high surface areas can be produced by the electrolytic reduction of metal compounds subjected to controlled physical pressure during electrolysis. When these plates are discharged as anodes in test batteries their capacities and ampere hour efficiencies are found to increase rapidly as the porosity increases. At porosities of 85-90%, high efficiencies were obtained for extremely high discharge rates over a range of temperatures extending down as low as  $-60 \text{ degrees C}$ . Similar results were obtained with high porosity cathodic active materials. The active materials thus tested included zinc, cadmium lead  $\text{Ag}_2\text{O}$ , and  $\text{AgO}$ , all of which were highly successful, thus indicating that the technique can be applied to a wide range of batteries and active materials.

1867. Langer, A., Patton, J. T.

114, 113, (1967)

### A Coullogravimetric Study of the Sintered Silver Electrode in 1-Molar Potassium Hydroxide.

Weighing of a sintered silver electrode while immersed in electrolyte during cathodic and anodic reaction reveals breaks in the weight change-coulomb curves. The different slopes can be explained by the volume change during phase transformation, affecting the buoyancy of the electrode. These breaks coincide with the potential changes of the plate, measured against a reference electrode.



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1868. Kober, F. P.

114, 215, (1967)

Infrared Spectroscopic Investigations of Charged Nickel Hydroxide Electrodes.

Through the use of deuterated samples of  $\text{Ni}(\text{OH})_2$  electrodes at various stages of charge, it has been possible to make definitive band assignments for the structures of the active material. The relative intensity of the band due to hydrogen bonding in the charged state is shown to be a measure of the electrochemical capacity of the system. The charging reaction gives rise to the formation of active oxygen sites (as defined by Aia) through a site alteration mechanism in addition to the formation of hydrogen bonded sites within the charged phase. The mechanistic and structural implications of these spectral data are discussed in detail.

1869. Aia, M. A.

114, 418, (1967)

Structure and Stoichiometry of Nickel Hydroxide In  
Sintered Nickel Positive Electrodes.

Differential thermal analysis (DTA) is shown to be a powerful tool in the study of the structure of electrochemically active materials. DTA was combined with chemical and x-ray diffraction analysis to follow both the electrolytic development in KOH solutions and the thermal decomposition of the charged state of sintered nickel electrodes impregnated with nickel hydroxide. The charged state contains active oxygen, insoluble potassium, water of constitution, and water of hydration. The electrochemical capacity is close to the electrochemical equivalent of the active oxygen formed on charging. The layer lattice is distorted and decomposes exothermically to NiO when heated above 100 degrees C.

1870. Weissman, E.

114, 658, (1967)

Structural Studies of Porous Electrodes.

Nondestructive techniques are described for the measurement of total electrode surface area, microporosity and pore size distribution, total porosity, and fraction of total porosity consisting of open pores. These measurements have been applied to a class of composite porous electrode structures based on platinum black, Teflon, and a metal screen current collector. They have been shown to correlate with electrochemical performance on the basis of exponential relationships of the type

$$i = a \exp (bS \text{ or } b \Sigma V)$$

where  $i$  is the current or limiting current density based on the geometric electrode area,  $S$  is the total (BET) surface area,  $\Sigma V$  is the cumulative micropore volume, and  $a$  and  $b$  are constants depending on the type of electrode and experimental conditions. The electrochemical



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performance of the electrodes was shown to increase with an increase in the percentage of total open (i.e., accessible) porosity consisting of micropores. It is not clear, at present, whether the relative importance of the micro- and macro-pore structures is actually conducive to maximum or asymptote-type of optimum structure, since no macropore size distribution data are now available. Within the micropore range of 25-350Å pore radius it was shown that the range 25-200 is performance-determining for the class of composite electrode that was studied.

1871. Hampson, N. A., Larkin, D., Morley, J. R.

114, 817, (1967)

### The Double Layer Capacitance in Aqueous Solution I Polycrystalline Silver.

There is however general agreement that during the early stages of electrode/electrolyte contact, pronounced capacity changes occur. Wagner observed a rapid reduction of double layer capacity on a freshly formed silver surface in contact with KCl solution. Gerischer and Fischer found that the double layer capacity on silver fell to one half of its initial value in about 5 min at room temperature. Although certain results might be explained by the adsorption of impurities from solution on to the electrode in general impurity levels have been satisfactorily controlled. Moreover initial changes in electrode activity have been reported for other metals, e.g., zinc, lead, and copper, and it is likely that pronounced changes in double layer structure occur on all metals during the early stages of electrode/electrolyte contact.

The purpose of this note is to present recent experimental findings of the double layer capacity of silver in sodium perchlorate solution.

1872. Hampson, N. A., Larkin, D.

114, 933, (1967)

### The Double Layer Capacitance in Aqueous Solution II Polycrystalline Cadmium.

Experiments with exchange reactions at solid cadmium electrodes have indicated interesting time dependencies. Discussion of these results has necessitated a knowledge of the double layer capacity-potential curves for cadmium and the position of the pzc. Although Russian workers had reported the results of differential capacity measurements on solid cadmium in KCl solution it was decided to redetermine the curves and to extend the results to NaClO<sub>4</sub> electrolytes. In this note the results of differential capacity measurements on flat polycrystalline cadmium in aqueous KCl and NaClO<sub>4</sub> electrolytes are reported.

1873. Baker, C. T., Trachtenberg, I.

114, 1045, (1967)

### Conductivity of KOH and KOH-ZnO Electrolytes from 36° to -66° C.

Currently, emphasis is being placed on the research of alkaline batteries using the negative zinc electrode, and more information is needed on the KOH and KOH-ZnO electrolyte systems which are used in such batteries. In this note data are presented on the specific conductivities of



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

various KOH and KOH-ZnO solutions as a function of temperature between 36° and -66°C and on the solubility of ZnO in these KOH solutions. These latter data are in agreement with those of other investigators.

1874. Malachesky, P., Jasinski, R., Burrows, B.

114, 1104, (1967)

### Impurity Effects in the Pre-Electrolysis of Caustic Electrolytes.

Pre-electrolysis is a common purification technique for aqueous solutions. However, detectable quantities of dissolved anode metal are found in caustic electrolytes, if one of the pre-electrolysis electrodes is allowed to reach the oxygen evolution potential. The reduction of O<sub>2</sub> on oxidized cadmium and the displacement of the H<sub>2</sub> evolution potential on gold are useful tests for this phenomenon. Holding the Pt anode at +500 mv (vs. DHE) or less prevents dissolution. Significant purification is accomplished on a high surface area platinum fuel cell electrode held  $\leq +300$  mv (vs. DHE). Some of the impurities adsorbed by the electrode are desorbed at +500 mv. In the purified electrolyte little activity for oxygen reduction was found on oxidized cadmium; the reaction on reduced cadmium is diffusion limited.

1875. Dirkse, T. P., DeWit, D., Shoemaker, R.

114, 1196, (1967)

### Silver Oxide Electrode Processes.

The cathodic and anodic overvoltages at a silver electrode were measured in a range of KOH concentrations of 20-45%. The values of these overvoltages undergo a change in 30-35% KOH. Similar changes or maxima or minima have been observed for other phenomena in KOH solutions, e.g., double layer capacitance. An attempt to account for these changes is made in terms of ion-pair association in concentrations greater than 35% KOH. This association is due to insufficient solvent for the normal hydration of the ions.

1876. Dirkse, T. P., DeWit, D., Shoemaker, R.

115, 442, (1968)

### The Anodic Behavior of Zinc in KOH Solutions.

The anodic behavior of zinc in strongly alkaline solutions was studied making special note of the limiting current density and of the overvoltage for the zinc/zincate reaction. The effect of temperature, KOH concentration, presence of zincate and amalgamation on these values was measured. Under the conditions studied, zincate ion diffusion away from the electrode controls the limiting current density. The overvoltage at amalgamated electrodes is that for the charge transfer reaction, while at nonamalgamated electrodes it is due to atom diffusion.



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1877. Tuomi, D., Crawford, G. J. B.

115, 450, (1968)

### The Nickel Positive Electrode II. Semiconduction and Electrode Performance.

The anodic oxidation of nickel hydroxide in pure lithium hydroxide electrolytes processes an n-type semiconductor. The anodic oxidation involves lithium migration into the active material. The beta phase is characterized at room temperature by Seebeck coefficients near  $-100 \mu\text{V}/^\circ\text{K}$  and electrical conductivities of 1 mho/cm. This is in contrast to the positive Seebeck coefficient for lithium nickelate.

1878. Dyson, W. H., Schreier, L. A., et al.

115, 566, (1968)

### Physical-Chemical Studies of KOH-ZnO Electrolytes.

Physical-chemical studies of the electrolyte system KOH-ZnO in the range 30-46% aqueous KOH are described. Vapor pressures at  $100^\circ$  -  $145^\circ\text{C}$  were obtained in sealed bombs equipped with gauges. Electrical conductivities of samples were measured at  $10^\circ$ ,  $25^\circ$ , and  $55^\circ\text{C}$ . ZnO solubilities over the range  $10^\circ$  -  $145^\circ\text{C}$  were determined by analysis of KOH solutions saturated with ZnO; a special solubility apparatus was constructed to obtain samples at temperatures above  $100^\circ\text{C}$ .

1879. Wales, C. P.

115, 680, (1968)

### Charging the Silver Oxide Electrode with Periodically Varying Current III. 60 cps Asymmetric A. C.

The discharge capacity of sintered silver electrodes in KOH solutions was improved 40-50% when the prior charge was made by a 60 cps asymmetric a.c. composed of two opposing half-wave currents  $180^\circ$  out of phase, rather than a constant charge current, both at the 20-hr rate in 35% KOH at  $25^\circ\text{C}$ . Commercial Ag-Zn cells containing similar silver electrodes gave capacity increases of 15-25% under the same conditions. Capacity depended on the proportion of charge and discharge components of the a.c. Capacity improvements were smaller when net charge current was at the 6-hr rate, when charge current was composed of 60 cps half-wave reverse current superimposed on constant charge current, or when the KOH concentration was increased. No significant improvement occurred when the charge with reverse current followed a series of discharges at the 1-hr rate.

1880. Dirkse, T. P., Shoemaker, R.

115, 784, (1968)

### Double Layer Capacitance of Zinc Electrodes in KOH Solutions.

The double layer capacitance of amalgamated and nonamalgamated zinc electrodes has been measured in a range of KOH solutions at room temperature. The presence of zincate ions and



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

of surface active materials modifies the capacitance values. There appears to be some correlation between the extent to which a surface active material modifies the double layer capacitance and its effectiveness in increasing the cycle life of the zinc electrode.

1881. Fleischer, A.

115, 816, (1968)

### The Solubility of Silver (II) Oxide in Alkaline Solutions.

The solubility of AgO in potassium hydroxide solutions has been reported by Dirkse and Wiers up to 5M KOH and by Hills up to 12M KOH. The authors of both papers indicated that the solubility curve as a function of KOH concentration at 25°C was the same as that for the solubility of silver (I) oxide, Ag<sub>2</sub>O. Amlie and Ruetschi indicated that there was an uncertainty with regard to the solubility of AgO. They considered the coincidence in the solubilities of the two oxides to be rather suspicious, citing that Dirkse et al. did not show that the dissolved species was bivalent. Subsequently Hills refers to the "proven presence of a higher valent species."

1882. Otto, E. M.

115, 878, (1968)

### Rates of Dissociation of Ag<sub>2</sub>O<sub>2</sub>.

The dissociation of Ag<sub>2</sub>O<sub>2</sub> into Ag<sub>2</sub>O and O<sub>2</sub> has been investigated over the temperature range from 22° to 100°C for the dry material, for water slurries, and for slurries in KOH solutions of concentrations from 1 to 13M. The method consisted in measuring the O<sub>2</sub> volume while the dissociation was progressing, and in most cases very smooth curves were obtained when the volume of dry O<sub>2</sub>, corrected to 0°C, 760 Torr, per gram of sample was plotted against time. Ag<sub>2</sub>O<sub>2</sub> in water had the lowest rate of evolution, dry Ag<sub>2</sub>O<sub>2</sub> had an intermediate rate, and Ag<sub>2</sub>O<sub>2</sub> in the high concentrations of KOH solution, such as are used in Ag-Cd cells, had the highest rate. The rates ranged from 0.0001 to 1.8 ml hr<sup>-1</sup> g<sup>-1</sup>.

1883. Wales, C. P.

115, 985, (1968)

### Charging the Silver Oxide Electrode with Periodically Varying Current IV. Intermittent Constant Current Reversals During Charge.

Sintered silver electrodes of the type used in storage batteries were charged by a constant current that was interrupted by periodic constant current discharges. Comparison to results from constant current charges showed a large capacity increase when the 20-hr constant charge current was reversed for 15 min out of every 60 min, but the total time required for a charge had increased greatly. Capacity could be improved a smaller amount, without charge time becoming excessive, by partly discharging the silver electrodes the first one or two times that potential reached a chosen value near the end of a constant current charge. In general, capacity improvement decreased as KOH concentration increased. Commercial silver-zinc cells always gave less improvement than the test cells.



ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

1884. Langer, A., Pantier, E. A.

115, 990, (1968)

A Coulogravimetric Investigation of the Zinc Electrode in Potassium Hydroxide.

The presented results obtained by weighing the zinc electrode in the electrolyte during the discharge cycle agree with data of others and explain why the capacity of the zinc electrode is a function of the amount of electrolyte used and roughly linearly dependent on the concentration of the potassium hydroxide up to about 10M. Previous results, that part of the zinc goes into solution, part is precipitated out as oxide or hydroxide, and that some adherent layer is formed which finally forces the potential of the plate to drop sharply, are substantiated on a more quantitative basis. The experiments also indicate that the relatively thick scale formed might not be the sole cause of the passivation phenomena.

1885. Hersch, P. A.

115, 1100, (1968)

Galvanic Monitoring of Battery Gases.

The rates of evolution of oxygen and hydrogen from a battery can be transduced continuously to an electric current for recording. A stream of nitrogen carries the evolved gases into a self-attenuating system with a galvanic-coulometric cell selectively activated by oxygen. Oxygen from the battery is monitored directly; hydrogen by a difference method invoking continuous combustion. The method may be used for studying charge acceptance, formation efficiency and omitting attenuation, for determining self-discharge, corrosion rate, and other battery-related data.

1886. Tvarusko, A.

115, 1105, (1968)

The Electric Resistivity of AgO

The electric resistivity,  $\rho$ , of powder AgO samples, made by the chemical oxidation of  $\text{AgNO}_3$ , was measured in situ up to 10 kbar.  $\rho$  increased linearly with decreasing AgO content of the samples ( $>70\%$ ). 63 AgO samples of 98.4% mean AgO content had a mean  $\rho$  of 59.3 ohm cm at 2.1 kbar. When Mg, Ca, Cd, In, Si, Y, Pd, Ni, or Co was added (as compounds) during the preparation of AgO,  $\rho$  of the sample increased. The addition of Hg, Ge, Sn, Pb, As, Sb, or Bi had a beneficial effect on  $\rho$  of AgO samples. Pb increased the length of the higher voltage plateau of AgO-Zn cells during discharge whereas Hg had no influence.

1887. Dirkse, T. P.

115, 1169, (1968)

Further Studies on the Double Layer Capacitance of Zinc in KOH Solutions.

In a recent report dealing with the double layer capacitance (dlc) of zinc electrodes in KOH solutions it was suggested that the lowering of this dlc may be related to improved cycle life of zinc electrodes, especially in silver-zinc batteries. Amalgamation, e.g., which improves the



## ELECTROCHEMICAL SOCIETY, JOURNAL OF (Cont.)

cycle life of zinc electrodes, also brings about a reduction in the double layer capacitance. This work has been continued and further results are reported here. Furthermore, a recent report on the cycle life of silver-zinc cells has made further comparisons possible.

1888. Wales, C. P., Simon, A. C.

115, 1228, (1968)

### Changes in the Microstructure of a Sintered Silver Electrode after Repeated Cycling at a low Current.

Cross sections of Ag electrodes were examined by optical microscopy. Most small particles present in an unused sintered Ag electrode were completely oxidized to AgO during the first charge, but electrode capacity then decreased markedly during the next few cycles at the 20-hr rate in 35% KOH. Slow discharges resulted in the formation of large granular Ag particles which did not oxidize as readily or extensively as small Ag particles. Voids were small and well distributed in the unused electrode, but with repeated cycling the voids became large as active material clumped. Grid corrosion occurred but did not impair performance.

1889. Cohen, G. L., Atkinson, G.

115, 1236, (1968)

### The Formation and Characterization of the Tetrahydroxy Argentate (III) Ion in Alkaline Solution.

When smooth silver metal is anodically oxidized in 12M KOH solution at 70 ma/cm<sup>2</sup>, a solution containing silver all in the +3 oxidation state results. The Ag (III) species was shown to be Ag (OH)<sub>4</sub><sup>-</sup> by a polarographic method involving the variation of half-wave potential with ligand concentration.



ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF

2000. Hosono, T., Matsui, M., Suzuki, K.

27, E104, (1959)

The Overpotential of The Cadmium Electrode.

The discharge reactions of cadmium electrodes in an alkaline solution have not yet been definitely established.

The outstanding features were observed in a previous work. In this work the transient phenomenon of discharge was measured for various conditions, and could be partially explained qualitatively and quantitatively.

2001. Yoshizawa, S., Takehara, Z., Matsui, M.

28, E9, (1960)

Electron-Microscopic Studies on Surface Structure of  
Cadmium Hydroxide Electrode.

Electron microscopic observation on the fine structure of a metallic oxide electrode surface is very important for the analysis of an electrode reaction mechanism. However, preparation of a reproducible replica with fidelity for electron microscopic observation on many metallic oxide electrodes used for the active mass of batteries is very difficult, and discussions on the reaction mechanism by electron microscopic observation have not been carried out yet. The new replica method for observation on a metallic oxide was applied for the experiments concerning the cadmium hydroxide electrode.

2002. Yoshizawa, S., Takehara, Z.

28, E26, (1960)

Changes of The Fine Structure of Cadmium Electrode Surface  
by Various Discharge Conditions.

In the previous paper, the results of electron microscopic observation on the surface structures of cadmium hydroxide electrodes were discussed. In this paper, the changes of fine structure of cadmium electrode surfaces by various discharge conditions are discussed in detail. Sample electrodes for electron microscopic observation were prepared in a nitrogen atmosphere in order to remove the changes of surface structure by self-discharge. However, cadmium hydroxide crystals may be enlarged or dissolved in the course of this operation which takes many hours; so samples not changed by growth and dissolution of crystals are obtained. Also, attention is paid to the uniformity of current distribution on cadmium electrode surfaces.



ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF (Cont.)

2003. Hosono, T., Matsui, M.

28, E170, (1960)

The Difference In The Reaction Mechanism of The Positive and Negative Plate of  
The Ni-Cd. Alkaline Battery and the Electrochemical Behavior of  
Electrodeposited Cadmium Electrode.

The positive and negative plates of nickel-cadmium alkaline batteries appear to possess some common characteristics in electrochemicals and crystallographicals. Prior to detailed study of the reaction mechanism of the negative plate, the difference of these plates was discussed with brief reference to the electrochemical behavior of electrodeposited cadmium electrode.

2004. Hosono, T., Matsui, M.

29, E37, (1961)

Studies on the Negative Plate of Ni-Cd Alkaline Batteries III. The Overpotential  
in Solid Phase of the Cadmium Electrode in Alkaline Electrolyte.

Our study on the mechanism of the discharge of cadmium electrodes in alkaline electrolytes has shown that the reaction process may be considered as occurring in the slow and quick ones. The former was reasonably explained on the basis that the primary product ( $\text{CdO}$  or  $\text{Cd}(\text{OH})_2$ ) reacts with the electrolyte and redeposits as  $\text{Cd}(\text{OH})_2$ . In this paper consideration is given of the electrochemical aspects of the quick process.

2005. Sugita, K.

29, E46, (1961)

Sintered Type Alkaline Storage Batteries III. Preparation and Cell Performance  
of The Positive Plate. (II) Influence of Lithium Hydroxide on its Durability.

It was suggested in the previous report, part 2, that  $\text{LiOH}$  added to the alkaline electrolyte might have influence on the durability of nickel positive plate. In this report, several positive plates were prepared, and one of these test plates was combined with two negative plates of pocket type which have larger capacity than the test plate. Cells thus constructed were repeatedly charged and discharged in cycles by the automatic apparatus and the influence of  $\text{LiOH}$  on the test plate was examined.

The change in the capacity was observed on every 100th cycle. Consequently, it was made clear that  $\text{LiOH}$  added to the electrolyte affects the durability of the positive plate remarkably. After the conclusion of a life test, the active materials in the test plates were examined by electromicroscopy and a counter-diffractometer. The action of  $\text{LiOH}$  upon active material was considered.



**ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF (Cont.)**

**2006. Yamashita, D., Takeuchi, Y.**

**29, E79, (1961)**

**Studies on The Sintered Type Alkaline Storage Batteries III. Neg. Plates  
Prepared by Vacuum Impregnation and Fusing Salt Impregnation.**

Plaques prepared by electrolytic nickel and commercial carbonyl nickel were impregnated with cadmium nitrate by vacuum and salt-fusing methods. The properties of these plates were examined.

**2007. Sugita, K.**

**29, E88, (1961)**

**Sintered-Type Alkaline Storage Batteries IV. Behaviors of Active Materials  
of The Cathode (1) Discharge Characteristics and Results  
of X-Ray Diffraction of The Cathode Plate.**

Powder and nickel screen were sintered in an  $H_2$  atmosphere according to the ordinary method, and nickel or copper plaques were prepared. The plaques were impregnated with  $CdCl_2$ , aq.,  $FcCl_2$  aq. and their mixture. After electrolytic reduction, they were washed and dried.

The cathode plates containing the active materials in the amount of 2 or 3 grams were prepared by repeating the procedure mentioned above. Batteries were constructed with one test plate and two anode plates of higher capacity. The batteries were put through repeated charge and discharge cycles and the discharge characteristics were examined.

**2008. Sugita, K.**

**29, E89, (1961)**

**Sintered-Type Alkaline Storage Batteries V. Behavior of The Active Metals of  
The Cathode. (2) Electronmicroscopic Observations and The Results  
of Thermo-Analysis of Active Materials of the Cathode.**

Preparation of the test plates and the tests by charge and discharge were carried out by the same methods as described in the previous report. Electronmicroscopical observation was carried out by the two-step replica method using M.M.A-A1.



ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF (Cont.)

2009. Sugita, K.

29, E92, (1961)

Discharge Characteristics of The Sintered-Type Alkaline Storage Batteries.

The preparing data of the experimental cells are given, and the discharge characteristics of the cells are shown. Relations between discharge currents and the capacities were measured at 30 degrees C on each cell. The discharge currents were 2A, 5A, 25A and 100A, respectively.

2010. Sugita, K.

29, E193, (1961)

Sintered-Type Alkaline Storage Batteries VI. Influence of Preparing Conditions Upon the Durability of The Sintered-Type Cadmium Negative Plate.

Capacity of the sintered-type cadmium negative plate decreases gradually with the repeated charge and discharge cycles. In this experiment, influences of the preparing conditions, such as sorts of cadmium salts for impregnation, specific gravities, current densities for reduction and sintering temperatures of plaques on the durability of the negative plate were examined, because it was considered that they have some connection with the plate performance.

Preparation of the plate was made by the usual method except in the impregnation of the active material; it was done under atmospheric pressure in this experiment. The impregnation were repeated 5 to 7 times and the weights of active material were 11 to 13 g.

One of the test plates and two of the pocket-type positive plates which had larger capacity than the negative plate were combined in a 500 cc glass vat. These plates were separated by a glass rod and the vat was filled with KOH aqueous solution. (sp. gr. 1.24 at 20 degrees C).

2011. Sugita, K.

29, E195, (1961)

Sintered-Type Alkaline Storage Batteries VII. Behavior of The Sintered Type Nickel Positive Plates.

A life test of the positive plate was previously carried out and the effect of lithium hydroxide on the plate was recognized. In the experiment, the capacity of the plate increased with repeating cycles, reaching a maximum at about the 200th cycle. But the capacity gradually decreased after that cycle. On the other hand, the capacity of the plate with ten grams per litre of lithium hydroxide plus a potassium hydroxide electrolyte was smaller than the one containing no additive agent. But its change in capacity was little and the life was fairly longer. These problems must be further examined.

This report describes the results of studies on these points.



2012. Yamashita, D., Yamamoto, Y.

30, E52, (1962)

**Studies on The Sintered-Type Alkaline Storage Batteries IV. Negative Plates  
of Sintered-Type Alkaline Storage Batteries  
Prepared by Fusing Salt Impregnation.**

Our new method of impregnating active material in negative plaques of Sintered-type Alkaline Storage Batteries is as follows. Plaques preheated at 80~260 degrees C for 10 minutes were quickly thrown into cadmium nitrate fused at 60 degrees C and kept for 5 min. After being reduced cathodically in 25% potassium hydroxide solution at 80 degrees C for 20 minutes, these plaques were heated at 80 ~ 260 degrees C for 30 min. and thrown into fused cadmium nitrate. Then electrolysis, heating, and throwing were repeated several times (but these plates were not heated after the last electrolysis). At single impregnation, the apparent availability of active material is fairly high at 80 degrees ~ 100 degrees C, but suddenly drops to the lowest value at 140 degrees C, and then increases over 200 degrees C.

2013. Hosono, T., Matsui, M.

30, E108, (1962)

**Studies on the Negative Plate of Ni-Cd Batteries IV. The Mechanism for The Formation  
and The Formula of The Primary Product Formed on a Cadmium Electrode  
During The Discharge Reaction.**

The discharge mechanism for a cadmium electrode has been investigated by us on the basis of the postulate that a primary product is formed. Furthermore, in this work the mechanism of the formulation and the formula of this primary product were studied in detail.

A cadmium electrode whose surface has been transformed into CdO by heating was discharged or self-discharged in an alkaline electrolyte under various conditions. In particular it was discharged with various impurities added to the electrolyte.

2014. Hosono, T., Matsui, M.

30, E109, (1962)

**Studies on the Negative Plate of Nickel Cadmium Alkaline Batteries V.  
The Influence of Impurities on Cadmium Plates of Alkaline Cell.**

Little information is available about the effect of various impurities on the performance of alkaline cell.

Cadmium negative plates (Pocket type) which involved such impurities as one each of Cu, Ag<sub>2</sub>O, Mg, MgO, CaO, HgO, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Tl<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Sn, Pb, PhO, Sb, S, Cr<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, Ni, NiO in active material and KNO<sub>3</sub>, KCl, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in electrolytes were examined under various conditions.

After fully formed, these plates were charged and discharged at low or high rates and the characteristic discharge curves were measured. Furthermore the plates were allowed to stand idle under fully charged condition for 850 hours and loss in capacity was measured in each case.



ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF (Cont.)

2015. Hosono, T., Matsui, M.

30, E109, (1962)

Studies on the Negative Plate of Nickel Cadmium Alkaline Batteries VI.

The Effect of Impurities on the Reaction Process during the Discharge of Cadmium Electrode.

In previous papers, the reaction mechanism for a cadmium electrode under discharge and the influence of many impurities on the electrode were described.

Two reaction processes were proposed.

- (1) Reaction process in solid phase (formation of primary product, active  $\text{Cd}(\text{OH})_2$ ).
- (2) Reaction process in liquid phase (primary product is converted to  $\text{Cd}(\text{OH})_2$  through the electrolyte).

2016. Yamashita, D.

31, 47, (1963)

Studies on Sintered-Type Alkaline Batteries VII. Effect of Cobalt on the Positive-Plate of Sintered Type Alkaline Storage Batteries.

The author studied the effects of cobalt on the positive plates of sintered-type alkaline storage batteries by the following experiments:

- (1) Charge-discharge curve of the active material of Ni-Co system.
- (2) Durability test (capacity change by repeating charge-discharge for long period).
- (3) Low rate charge test.
- (4) X-ray diffraction diagram and electronmicrophotograph of active material.

According to these experimental results, charge-discharge potential dropped with increasing cobalt content. Active material seems to be a solid solution  $(\text{Ni, Co}) (\text{OH})_2$  up to 20% Co, but mixtures of  $(\text{Ni, Co}) (\text{OH})_2$  and  $\text{Co}(\text{OH})_3$  over 30%. The availability of active material increased with only a 5% addition of cobalt.

Capacity drop by charge-discharge for long periods and by low rate charge may be essentially prevented by the addition of cobalt.

This behavior of cobalt is probably due to the formation of the solid solution  $(\text{Ni, Co}) (\text{OH})_2$  in active material.

2017. Yoshizawa, S., Takehara, Z.

31, 91, (1963)

Electrode Phenomena of Silver-Silver Oxide System in Alkaline Batteries.

Electrolytic behavior of the silver-silver oxide system in an alkaline battery and the effects of the addition of small quantities of various metals to the silver electrode were studied by utilizing electron microscopic and X-ray diffraction methods and oscilloscopic technique for the determinations of decay and growth of overpotential and current-potential relations. It was shown that during charge,  $\text{Ag}_2\text{O}$  and  $\text{AgO}$  were followed by the expansion of the Ag crystal owing to a diffusion of oxygen ion; on discharge, the reverse process should occur.



ELECTROCHEMICAL SOCIETY OF JAPAN, JOURNAL OF (Cont.)

2018. Yoshida, T., and Koseki, K. 35, 24, (1967)

Extended Equation for Current Distribution in Rectangular Cells (Part 1).

An extended equation of macroscopic current distribution at the plane cathode in a rectangular cell has been introduced, from the geometrical point of view with the intention of achieving at least some degree of actual practicability.

The solution of this problem has been found by means of conformal mapping, as reported by C. Wagner, but this study dealt with cases where no edge of the horizontal electrodes reached the side wall, and the cathode was broader than the anode, under the assumption that polarization could be disregarded.

Results substantially in agreement with Ishizaka's equation or Wagner's results can be obtained by inserting appropriate boundary conditions into the extended equation introduced by the authors.

2019. Koseki, K., Hashimoto, Y., Yoshida, T. 35, 88, (1967)

Extended Equation for Current Distribution in Rectangular Cells. (Part 2)

In a previous paper, an extended equation for macroscopic current distribution at the plane cathode in a rectangular cell, under the assumption of negligible polarization was introduced.

Furthermore, a modified equation has been introduced in relation to current distribution under the influence of the distance between the edge of the cathode and a side wall.

Results of the theoretical analysis are compared to the experimental data obtained through accurate weighing of electrodeposits and observation of equipotential lines in the neighborhood of the cathode.

2020. Brenet, J. 35, 118, (1967)

Metal Oxides of Batteries.

From the known results about classical oxides used in secondary and primary cells, we tried to bring out general properties for all oxides and to relate electrochemical properties to superficial energy levels or to other physical and chemical properties.

It seemed to us necessary to state precisely in what directions it could be considered to develop some new investigations about oxides of a single metal or of several metals in order to try to increase the energetic possibilities of cells.

2021. Koseki, K. 36, 226, (1968)

Extended Equation for Current Distribution in Rectangular Cells. (Part 3)

Previous papers have dealt with the derivation, under the assumption of negligible polarization, of an equation for macroscopic current distribution at the plane cathode in rectangular cells and of a modified form of this equation taking into account the distance between the edge of the cathode and the side wall.

A further useful equation is introduced in this paper in due consideration of electrolytic polarization, where the mathematical analysis has been conducted based on the integral form shown by Wagner. Making use of the above equation, the optimum condition for uniform current distribution is discussed in relation to the practical case with known polarization characteristics at the cathode.



**ELECTROCHEMICAL SOCIETY OF SOUTHERN CALIFORNIA\***

2100. Menard, C. J.

2, 75, (1966)

**Recent Development in Porous Structures for Nickel Hydroxide Electrodes.**

Porous structures, made by sintering nickel powders of irregular particle shape onto a nickel-plated support, are widely used in the production of nickel electrodes for nickel-cadmium batteries.

A Study was made of the characteristics of sintered plates prepared from nickel powders of various known densities. Particle size distribution and shape of the powder particles, shrinking during sintering, and electrical resistivity, porosity and pore size of the sintered plaque were investigated. Properties of the powder and the sintered plaque were correlated with their performance in the sealed cell.

The results indicate that efficiency of the active material of nickel electrodes increases with higher density powders.

2101. Belove, L.

2, 115, (1966)

**The Cadmium-Cadmium Coulometer—Its Operation and Practice.**

High rate charging and discharging of nickel-cadmium batteries may, under certain conditions, present problems. The rapid rise in the voltage of the cadmium-cadmium coulometer is utilized to reduce the current during overcharge (and, likewise, near the end-of-discharge) to a point where the battery can easily cope, thus ensuring long battery life as well as a very fast charging and high rate discharging capability. Coulometer and coulometer battery circuitry principles are described.

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\*Symposium held by the California-Nevada section of the Electrochemical Society on December 2, 1966 (entitled "Advances in Battery Technology").



## ELECTROCHEMICAL TECHNOLOGY

2200. Selis, S. M., Russell, C. R.

1, 77, (1963)

### An Analytical Representation of The Discharge Characteristics of Commercial Secondary Batteries.

The equation of Peukert has been applied to express discharge time and delivered capacity as a function of constant discharge current. Analytic relationships have been developed successfully for modern lead-acid batteries as well as for several secondary batteries with alkaline electrolytes.

Relationships also have been derived which relate mean terminal voltage to discharge current. It is therefore possible to express delivered energy as a function of current. The calculated values are in satisfactory agreement with the energy value as determined experimentally.

2201. Simon, A. C.

1, 82, (1963)

### Microscope Techniques for The Study of Electrochemical Processes.

Special techniques and apparatus, applicable to microscopy, that have been successfully used by the author in the study of corrosion, cell reactions and the analysis of electrode products, are discussed. Methods are given for preparing samples for examination, for constructing various types of microcell and for obtaining analytical samples from very small areas.

2202. Wilder, D. R.

1, 172, (1963)

### Progress In Sintering.

Sintering is broadly defined as all aspects of the adhesion, densification, shrinkage and consolidation accompanying the reduction in surface energy of a powder compact during application of heat and/or pressure. The process of sintering is then further divided into the initiation, material transport and grain growth-recrystallization stages. A general review is made of each of these stages, noting typical work which has contributed to progress in each area involved.

2203. Howard, P. L.

1, 272, (1963)

### The Sealed Silver-Cadmium Battery.

Recent satellite requirements for 90- to 100-min cycles of a 30- to 40-min discharge and a 60- to 70-min recharge necessitated the development of a new design: a sealed silver-cadmium battery which could be recharged during this period. A report of this development and on cycling results is given here. At present, over 7000 cycles have been obtained at 50%-capacity discharge in a 100-min cycle of 35 min of discharge and 65 min of recharge. A discussion of charging characteristics and voltages is given. This system makes it possible to achieve a sizable decrease in the weight and volume of a battery to be used in a satellite regime.



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

2204. Salkind, A. J., Canning, H. J., Block, M. L. 2, 254, (1964)

### Measurement of Pore Size and Surface Area of Porous Electrodes by Nondestructive Means.

The surface area and pore size distribution of powders have historically been measured by means of gas adsorption apparatus operating on the BET principle. The apparatus has been modified so that these measurements can be made on electrodes of various geometries by non-destructive means. This made possible the reuse of electrodes for electrochemical purposes after the determination of surface area and, therefore, the observation of surface area change with use on the same electrode. Measurements have been made on sintered nickel plaques, electrodes from nickel-cadmium cells, porous graphites, fuel cell electrodes and nonmetallic porous materials.

2205. Metzger, Jr., W. H., Sherfey, J. M. 2, 285, (1964)

### Electrochemical Calorimetry III. Thermal Effects of Nickel-Cadmium Batteries.

Calorimetric measurements were made during various charge-discharge cycles of nickel-cadmium cells proposed as satellite power sources by the National Aeronautics and Space Administration (NASA). Typical curves of heat changes as a function of time during operation are shown and discussed. The heat of reaction of oxygen with the constituents of the cell was measured and agreement was obtained with the literature value for the heat of formation of cadmium oxide.

2206. Hampson, N. A., Tarbox, M. J., Lilley, T., Farr, J. P. 2, 309, (1964)

### The Passivation of Vertical Zinc Anodes in Potassium Hydroxide Solution.

The passivation of vertical zinc anodes has been studied as function of current density, temperature and potassium hydroxide concentration. Results conform to the equation,  $i - i_j = k t^{-1/2}$ . Results are reproducible providing that  $t$  is not large enough for the establishment of complicated patterns of turbulent flow that disturb the evenness of the anode current density. Interpretations of  $k$  and  $i_j$  are given. Practical systems are mentioned.

2207. Turner, D. R. 2, 313, (1964)

### The Effect of State-of-Charge of the Cadmium Electrode on Oxygen Recombination in Sealed Nickel Cadmium Cells.

The rate of oxygen recombination in sealed Ni-Cd cells on overcharge was found to be directly proportional to the amount of metallic cadmium on the negative electrode, i.e., the state-of-charge of the cadmium electrode. Good agreement was found between oxygen recombination obtained from steady-state overcharge and pressure decay measurements when the



## **ELECTROCHEMICAL TECHNOLOGY (Cont.)**

state-of-charge was lowered. There is evidence that cadmium distribution on the electrode is an important variable. Cells which recombine oxygen poorly can be improved considerably by increasing the state-of-charge of the cadmium electrode.

2208. Brodd, R. J., DeWane, H. J.

3, 12, (1965)

### **Impedance of Sealed Nickel-Cadmium Dry-Cells.**

The impedance of various sizes of nickel-cadmium dry cells was measured as a function of frequency between 50 cps and 50 kcps. The effects of aging, discharge and temperature on the impedance of the cells were determined. The temperature coefficient of electromotive force was determined for some cells. The discharge characteristics of AA-size nickel-cadmium and Leclanché cells were compared on two standard tests. It was found that the impedance of nickel-cadmium cells increased during discharge, decreased about 2-3%/degrees C increase in temperature, increased slightly during storage, was less for larger cells, and that for cells of equal rated capacity the sintered type had a smaller impedance than the pressed-powder type.

2209. Tracey, V. A., Williams, N. J.

3, 17, (1965)

### **The Production and Properties of Porous Nickel for Alkaline Battery and Fuel Cell Electrodes.**

Loose sintering, slurry, roll compacting and pressing techniques have been surveyed for carbonyl nickel powder, considering porosity, electrical resistivity, strength and pore spectrum as the most useful parameters for both applications. High porosities, 70-90%, are preferred for alkaline batteries, and the best procedures are loose sintering and slurry techniques, although roll compacting is feasible using a spacing agent. Fuel cell electrodes require a narrow pore spectrum, and roll compacting or pressing is preferred, but loose sintering and slurry techniques can be used in conjunction with these techniques for the production of dual porosities.

2210. Bauer, P.

3, 43, (1965)

### **Pressure Characteristics of Sealed Nickel Cadmium Cells.**

Build-up of excessive pressures in sealed nickel-cadmium cells is investigated by a balanced pressure technique and by low-rate overcharge methods. The appearance of abnormally high pressures is shown to be related to the appearance of terminal voltages above 1.50v and to the open-circuit stand time of the cells. A mechanism for the deterioration of pressure-performance with stand time is postulated and a method of verification suggested.

2211. Tudor, S., Weisstuch, A., Davang, S. H.

3, 90, (1965)

### **Application of Autoradiographic Techniques to Battery Research.**

Autoradiographic techniques have been applied to battery research. Such techniques provided evidence of a sulfate barrier layer between grids and active material, associated with



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

severe capacity losses, in positive plates of thin-plate, lead-calcium grid batteries operated on a modified float regime. The influence of  $\text{H}_3\text{PO}_4$  electrolyte additive in minimizing the formation of such detrimental sulfate layers was determined autoradiographically. The techniques developed are applicable to studies of other electrode systems, provided suitable isotopes are available.

2212. Dirkse, T. P.

3, 106, (1965)

### The Measurement of Zincate Diffusion Through A Membrane.

The diffusion rate of zincate ions through a membrane has been determined by a method using voltage measurements and another method using radioactive zinc isotope. The voltage method is faster, but does not give as good reproducibility as the radioactive methods. Measurements show that Fick's law of diffusion is applicable to this zincate diffusion.

2213. Snyder, R. N., Lander, J. J.

3, 161, (1965)

### Rate of Hydrogen Evolution of Zinc Electrodes in Alkaline Solutions.

A study was made of some factors that affect the rate of self-discharge of the Zn electrode in alkaline solutions. Hydrogen evolution in cells containing 5, 15, 30, 40 and 45% potassium hydroxide as electrolyte was measured at 100 degrees F. Other temperatures were studied. Electrolyte solutions saturated with ZnO were also evaluated. Charged zinc electrodes with 1, 2 and 4% HgO added were studied in conjunction with plain and amalgamated grids. Gassing rates were observed over a 30-day interval. Results indicate that the gassing rate varied inversely with electrolyte and HgO concentration and directly with temperature, while ZnO saturation and grid amalgamation had little effect. The data obtained are expected to be useful in scaled silver oxide-zinc battery design.

2214. Dirkse, T. P.

4, 163, (1966)

### Cycling Characteristics of The Silver Electrode in Alkaline Solutions.

A study has been made of the effect of high current densities at room temperature on the cycling behavior of sintered silver electrodes in alkaline solutions. Further work has been carried out at temperatures below freezing. The silver electrode does not charge at 100% efficiency at high current densities at room temperature.

2215. Rüetschi, P., Ockerman, J. B.

4, 383, (1966)

### Sealed Cells With Auxiliary Electrodes.

Conventional secondary and primary batteries may be operated in a hermetically sealed condition, even if containing excess electrolyte forming a free liquid bath, by utilizing auxiliary



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

electrodes which are designed to consume hydrogen or oxygen gas electrochemically and which are held for this purpose at fixed half-cell potentials. Using solid-state diodes as potential-regulating means, unidirectional current flow to the auxiliary electrode is achieved rendering the latter specifically selective to either electrochemical oxidation or reduction in the desired potential range. This innovation relieves the battery electrodes from the function of gas removal as in ordinary sealed cells and thus permits cell designs with higher electrolyte content and associated higher energy density.

2216. Kober, F. P.

4, 423, (1966)

### An Electrolytic Impregnation Method: Nickel Hydroxide Electrode.

A method is described whereby a conducting porous matrix is impregnated electrolytically with nickel hydroxide. Impregnation is achieved by making the porous plaque anodic in an ammine nickel formate solution. Use of a current-interruption technique, as opposed to continuous d-c polarization, makes the degree of impregnation a linear function of time. Also, the method eliminates the need for cathode polarization in a caustic solution after impregnation. Plaques impregnated in this manner show excellent voltage characteristics and are suitable for use as positive electrodes in high-capacity, nickel-cadmium batteries.

2217. Atkinson, G. S.

4, 431, (1966)

### A Short History of The Jungner Nife Nickel-Cadmium Battery.

Toward the end of World War I, the Swedish Jungner Company, under encouragement from the British Admiralty, decided to develop their product outside Sweden and, for this purpose, the company of Nife Batteries Ltd., was formed at Redditch, England. As I had the good fortune to be given this task, this paper falls naturally into two parts: the first, prior to 1919, is based on internal documents of the Jungner and Nife Companies and on information given to me by colleagues who had worked with Dr. Waldemar Jungner; the second part, from 1919 onward, is matter which falls within my own personal experience.

2218. Gottlieb, M. H., Willis, T. H.

4, 515, (1966)

### Operating Characteristics of the Sealed Nickel Cadmium Batteries at Low Temperatures.

The performance of an experimental sealed nickel-cadmium cell made at Bell Telephone Laboratories was studied over the temperature range -40 degrees to +77 degrees F in order to determine the energy storage limitations, discharge capability, and overcharge capability at low temperatures. It was found that evolution of hydrogen gas occurred during the charging periods of the first cycles run at progressively lower temperatures. At -40 degrees F, there is a marked lowering in cell discharge midpoint voltage and cell capacity. Nearly half of the lowering of discharge voltage was found to be due to IR drop at the positive electrode. The decrease in



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

capacity and discharge voltage is not serious at temperatures down to  $-30$  degrees F. The evolution of hydrogen gas can lead to the irreversible development of high pressures and to reduction of cell capacity.

2219. Lifshin, E., Weininger, J. L.

5, 5, (1967)

### Electronic Microbeam Probe Analyses of Nickel Cadmium Battery Plates.

The emergence of electron probe microanalysis as a tool for metallurgical studies has made it possible to view battery plates with this new experimental technique. This method of analysis is applied to new and used negative electrodes of the nickel-cadmium cell. X-ray and electron distribution images from surfaces and cross sections of porous electrodes are shown, illustrating the advantages and limitations of the method.

2220. Gottlieb, M. H.

5, 12, (1967)

### Charging Behavior of Cadmium Hydroxide Electrodes at Low Temperatures.

It has been observed that the charge acceptance of cadmium hydroxide electrodes is markedly decreased during the first charge at low temperatures ( $1 \leq 0$  degrees F), following cycling at 77 degrees F, but recovers to normal on subsequent low-temperature charges. With constant current charging this first low-temperature charge is characterized by an abrupt shift in the potential, from the region of that usually associated with charging, to the region for hydrogen evolution, after only a fraction of the capacity of the electrode has been exhausted. The remainder of the charging of the electrode takes place, along with hydrogen evolution, at the more negative potentials. The parameters which affect this phenomenon were studied; these include the treatment of the electrode at 77 degrees F, the nature of the transition to low temperature. The value of the low temperature, the magnitude of the charging current, and the type of charging, i.e., constant current or constant potential. The data could be satisfactorily interpreted on the basis that the electrochemical oxidation of cadmium at 77 degrees F leads to formation of cadmium hydroxide in a state which is not readily reducible at low temperature, while oxidation at low temperature leads to a formation of cadmium hydroxide in a state in which it is readily reducible at the low temperature. The different states of the cadmium hydroxide could result from the effect of temperature on the precipitation of the soluble complex cadmium ion which had been previously postulated as an intermediary in the electrochemical oxidation process. Potentiostatic experiments indicate that the process which limits the low-temperature charging of cadmium hydroxide formed at 77 degrees F is not electrochemical in nature. This reduced first low-temperature cycle charge acceptance was apparently responsible for the development of significant pressures of hydrogen in sealed nickel-cadmium cells which had been reported earlier.



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

2221. Dirkse, T. P.

5, 18, (1967)

### Constant-Potential and Constant-Current Charging of Silver-Cadmium Cells.

The constant-current and constant-potential charging of a silver-cadmium cell has been studied using two reference electrodes, one for each working electrode. The sum of the individual electrode potentials was compared with the measured cell voltage. At charging rates of 3 hr, the measured cell voltage is affected by  $\text{OH}^-$  ion concentration gradients as well as by the state of charge of the electrodes.

2222. Okinaka, Y., Turner, D. R.

5, 67, (1967)

### Anodic Corrosion of Nickel Sinter in Positive Electrodes of Nickel Cadmium Batteries Containing Carbonate.

The charge capacity of sealed nickel-cadmium cells using sintered nickel plates was found to increase considerably when the cells were overcharged at a high rate after addition of a sufficient amount of carbon dioxide. A large-capacity increase occurs also under flooded conditions if the nickel hydroxide plate is subjected to repeated charge-discharge cycles or prolonged overcharge in concentrated potassium carbonate, followed by cycling in potassium hydroxide. The capacity increase has been found to be due to anodic corrosion of the nickel sinter to trivalent nickel. The corrosion occurs only with impregnated plates and not with bare, unimpregnated nickel sinters. Mechanism of the corrosion reaction is discussed in this paper. A practical procedure is given for the preparation of high charge capacity plates by utilizing the corrosion reaction.

2223. Niedrach, L. W., Tochner, M.

5, 270, (1967)

### Some Observations Concerning the Use of Low Frequency Interrupter Techniques in The Studies of Fuel Cells and Batteries.

While low frequency (<60-cps) interrupter bridges can serve admirably for the study of fuel cells and batteries, they are not universally applicable. Anomalous results can be obtained when polarizations having short time constants relative to the bridge frequency are encountered. Several effects symptomatic of a malfunctioning system are discussed, and methods of monitoring to obtain the most reliable information are presented.

2224. McHenry, E. J.

5, 275, (1967)

### Electrochemical Precipitation of $\text{Ni}(\text{OH})_2$ into Porous Electrodes.

Conventional methods for the impregnation of porous electrodes for use in Ni-Cd batteries are complex, time consuming, and expensive. In addition, these methods are not suited to continuous automatic processing. A simple, rapid, one-step process has been developed which is



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

capable of producing reproducible electrodes. Active material is deposited directly into the pores of the sintered Ni plaque by cathodic precipitation from acid  $\text{Ni}(\text{NO}_3)_2$  solution. Electrodes have been impregnated by this process in as little as 5 min with amp-hr capacity reproducibility of  $\pm 2\%$ . These electrodes have performed well in sealed cells under stressed cycling conditions.

2225. Dirkse, T. P.

5, 301, (1967)

### Silver Deposition on Battery Separators.

One of the problems associated with a silver-alkaline battery is the solubility of the silver oxides in the KOH electrolyte. Because of this, silver can be transported away from the silver electrode and deposited on the negative electrode. This latter effect leads to local cell action and self-discharge of the negative electrode.

Separators have been used to minimize this transport of silver. Cellulosic materials have been widely used for this purpose. However, as new materials become available, it is highly desirable that relatively quick methods be available to determine whether such new materials can effectively serve as a separator in a silver-alkaline battery. One of the requirements of an ideal separator is that it prevent the transport of dissolved silver oxides. A method has been devised for measuring the rate of silver diffusion through these separators. It was with the use of this method that the following results were obtained. A solution of 45% KOH containing dissolved  $\text{Ag}_2\text{O}$  with some  $\text{Ag}^{110\text{m}}$  added to it was placed on one side of the separator and a 45% KOH solution was placed on the other side. The radioactivity of each solution was measured from time to time during the run. This served as the analytical method for determining the amount of silver.

2226. Bogenschütz, A. F., Krah, P., and Schulz, J.

5, 405, (1967)

### The Influence of Sinter Temperature on the Capacity of Silver Electrodes.

Sintered silver specimens are used as high-capacity electrodes in galvanic cells. Their electrical properties depend to a great extent on the production parameters. The present paper reports on the influence of sintering temperature on the specific electrode capacities. For the experiments, dendritic silver powder was used because it was discovered in preliminary experiments that spheroidal silver powder provides approx 20% lower capacity. The grain size of the dendritic powder used for our experiments was approx  $37\mu$  in general. The BET surface of the powder before sintering was  $0.16 \text{ m}^2/\text{g}$ . Smaller grain sizes of  $< 28\mu$  yielded sintered parts having a high initial capacity around 400 ma-hr/g though it dropped to approx 300 ma-hr/g after some cycles.

2227. Farr, J. P. G. and Hampson, N. A.

6, 10, (1968)

### The Anodic Behavior of Cadmium and Lead in Alkali.

The anodic behavior of cadmium and lead in alkaline solution has been investigated. The metals develop surface films well before the potential rises to that for oxygen evolution at cadmium



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

anodes and for the transition from the Pb (II) to the Pb (IV) oxidation state of lead anodes. No simple law was found relating passivation time and current density. For cadmium, the grain size of the passive layer was influenced by the current density and electrolyte concentration. Comparison of the metals is made with zinc. Among the three metals, formation of surface films during the "active" regions of polarization corresponded to the solubilities of the anodic products in the electrolyte.

2228. Black, R. G., Pentacost, J. L. and Moore, H. S.

6, 20, (1968)

### Flexible, Thin-Film Nickel-Cadmium Batteries.

This paper presents the results of a study to develop and fabricate flexible nickel-cadmium batteries. Information presented includes chemical and electrochemical electrode fabrication processes for both the nickel and cadmium electrodes, flexible packaging techniques for use with the battery, and preliminary charge-discharge characteristics for the completed units. With the developed processes, flexible nickel cadmium batteries of 20 in.<sup>2</sup> and less than 0.010 in. thick were produced with capacities to deliver 100 ma for 1 hr at a potential above 1v.

2229. Sherfey, J. M., Halpert, G., and Tiller, S. E. D.

6, 25, (1968)

### A New Technique for Measuring the Internal Pressure of Sealed Electrochemical Cells.

A technique is described for measuring the internal gas pressure of sealed secondary electrochemical cells. In use, such cells are ordinarily restrained by a clamp or restraining device. The internal gas pressure can be determined by using a load cell to measure the force exerted by the secondary cell on this clamp.

2230. Hamlen, R. P., McQuade, J. M., and Siwek, E. G.

6, 83, (1968)

### Silver-Zinc Cells with Electrolytically Deposited Calcium Hydroxide Separators.

One of the problems associated with silver-zinc cells is the migration of colloidal or soluble silver oxides away from the silver oxide electrode. This silver leads to the breakdown of organic separators and possibly to an increase in the self-discharge of the zinc electrode. One method of decreasing the silver loss rate appears to be to coat the silver oxide electrode with an adherent layer of a relatively insoluble inorganic material. This can be accomplished conveniently by electrolytically depositing calcium hydroxide from a calcium acetate solution, with the silver oxide electrode as the negative electrode (cathode) and an inert positive electrode. Hydroxide ion, which is produced by either hydrogen evolution and/or silver oxide discharge, causes precipitation of calcium hydroxide within and on the silver electrode. The calcium hydroxide film formed is relatively hard and durable, although it can be chipped off readily with a sharp object. The film thickness can be controlled within limits by varying the current density and electrolyte concentration, but beyond a certain time the voltage at constant current changes sharply as the film becomes



## ELECTROCHEMICAL TECHNOLOGY (Cont.)

less permeable. The silver oxide electrodes coated in these experiments were of two types: commercial electrodes from silver-zinc secondary cells, and compacted divalent silver oxide electrodes for low-rate primary cells.

2231. Kerralla, J. A., and Lander, J. J.

6, 202, (1968)

### Effect of Surfactant Additions to the Zinc Plate on Cycle Life Performance of Secondary Silver Oxide-Zinc Cells.

Several surface active agents, including two variations of Emulphogene, Gantrez AN-169, cellulose gum, Igepal CO-730, and Modified Polyethoxy Adduct, were tested for their capability of increasing cycle life of zinc plates in secondary silver oxide-zinc cells. Cycle life increases of 50-80% were achieved by utilization of concentrations of 0.15-1.0% Emulphogene BC-610 in the zinc plate formulation.

2232. Brodd, R. J.

6, 289, (1968)

### Comments on Current Distribution in and on Porous Electrodes.

The various factors which influence current distribution are discussed and related to their effect on practical cell designs. The importance of completely defining the system of interest from a thermodynamic and reaction kinetics standpoint is stressed. A nondimensional parameter is defined and related to the nonuniformity of current distribution on the exterior surface of an electrode. The effect of a bipolar and other special constructions to improve the uniformity of current distribution is discussed. The marked leveling influence of polarization on the exterior and interior current distribution is noted. The effects of variation in electrode and electrolyte resistivity, exchange current density, current density, and electrode thickness are related to the reaction distribution in the interior of porous electrodes and to the effectiveness of a porous electrode in improving electrode performance. Some of the problems associated with the application of porous electrode theory to practical systems are pointed out.

## ELECTROCHEMISTRY AND ELECTROCHEMICAL ENGINEERING\*, ADVANCES IN

2300. Milner, P. C., Thomas, U. B.

5, 1, (1967)

### The Nickel-Cadmium Cell.

Nickel-cadmium storage batteries have been in use for more than half a century; since World War II, new design principles have been introduced which have greatly extended their usefulness. Although much remains to be understood in this system, it seems pertinent at the present time to examine what is known of the physical chemistry of the individual processes taking place within the cell and to indicate how some of the observed properties of the system in its more highly developed forms may arise.

For this purpose, detailed consideration is given to the electrochemistry of the individual components, the electrolyte and the positive and negative electrodes, and, while primary attention is directed to the more fundamental aspects of the behavior of the electrodes, some emphasis is placed on their physical preparation and construction as background for the understanding of practical systems. Cell construction and operating characteristics are treated briefly and those aspects of cell behavior that are presently amenable to analysis are examined.

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\*Edited by C. W. Tobias and P. Delahay, published by Interscience (1967).



## ELECTROCHIMICA ACTA

2400. Briggs, G. W. D.

1, 297, (1959)

### An Instrument for the X-ray Diffraction Study of Electrodes.

An easily constructed reciprocating device for the X-ray examination of working electrodes is described, and an example is given of its application to the study of electrodeposited layers.

2401. Sanghi, I., Visvanathan, S., Ananthanarayanan, S.

3, 65, (1960)

### Polarization Studies on Cadmium By Galvanostatic and Potentiostatic Technique.

The anodic polarization of cadmium in alkaline solutions has been studied under constant-current conditions. The potential may rise from about -0.9 V (vs. Hg|HgO|N KOH) to as much as 0.4 V on passivation; there appears to be more than one arrest in the polarization curves. Preliminary study of the effect of stirring indicates that it may hasten the transition in dilute solutions and delay it in concentrated solutions.

Potentiostatic studies in the range -1.2 to +1.2 (vs Hg|HgO|N KOH) have shown that hydrogen is cathodically evolved at -1.0 V; then, in the first truly active region (ca. -0.86 V), the main reaction is the formation of  $\text{Cd}^{2+}_{\text{aq}}$ ; after passivation (ca. +0.70 V) it changes to oxygen evolution. Potentiostatic techniques reveal intermediate stages, undisclosed by constant-current methods, of pseudo-passivation and current-plateau regions, in which the passivating layer thickens, controlled by high-field cation transport.

The results are briefly considered with special reference to the techniques adopted and results recently obtained by others.

2402. Yoshizawa, S., Takehara, Z.

5, 240, (1961)

### On Electrode Phenomena of Cadmium in the Alkaline Battery: The Discharge Mechanism.

The discharge mechanism of the cadmium electrode in the alkaline battery was examined by means of electron microscopy, X-ray and electron diffraction, observation of decay and growth of overpotential and current/potential relations. Cadmium seems to be transformed to cadmium hydroxide through an intermediate product, probably (from electron microdiffraction after discharge at low temperature in dilute potassium hydroxide solution) cadmium oxide. This dissolves as the complex ion ( $[\text{HCdO}_2]^-$ ) and then deposition of cadmium hydroxide on the electrode surface takes place. The overpotential is largely caused by ionic migration in the intermediate layer, which may be explained by the current/potential relation and the decay and growth of overpotential.



## ELECTROCHEMICA ACTA (Cont.)

2403. Lukovtsev, P. D., Slaidin, G. J. 6, 17, (1962)

### Proton Diffusion Through Nickel Oxide.

The diffusion rate of protons through a nickel-oxide film prepared by anodizing one side of a nickel foil has been determined from the increase in the anodic current necessary to maintain the oxide film in an alkaline solution at a constant potential after switching on cathodic polarization on the other side of the foil.

The diffusion rate of protons rises with increase in the oxide-film potential.

2404. Briggs, G. W. D., Wynne-Jones, W. F. K. 7, 241, (1962)

### The Nickel Hydroxide Electrode; The Effects of Aging. I. X-ray Diffraction Study of The Electrode Process.

Structural changes during the anodic oxidation and cathodic reduction of nickelous hydroxide have been observed by direct X-ray examination of electrodes, combined with powder photography and optical microscopy. The tendency towards persistence of texture and lattice structure during anodic oxidation was confirmed by comparison of the processes for freshly prepared and for aged electrodes. The diffraction evidence is shown to imply the formation of a series of nearly related layer structures rather than of distinct crystalline phases.

2405. Briggs, G. W. D., Stott, G. W., Wynne-Jones, W. F. K. 7, 249, (1962)

### The Nickel Hydroxide Electrode; The Effect of Aging. II. Changes in Electrochemical Behavior.

Polarization curves for the anodic oxidation and cathodic reduction of  $\text{Ni}(\text{OH})_2$  electrodes at constant current have been obtained, and also Tafel curves for the anodic process. A comparison is made between the electrochemical behavior of freshly prepared and of recrystallized  $\text{Ni}(\text{OH})_2$  layers, and the extent to which the differences may be correlated with structural changes in the solid phase is discussed.

2406. Benson, P., Briggs, G. W. D., Wynne-Jones, W. F. K. 9, 281, (1964)

### The Cobalt Hydroxide Electrode. II. Electrochemical Behavior.

Polarization and decay curves have been obtained for cathodically prepared cobalt hydroxide layers in alkaline solution. Their electrochemical behavior is discussed and contrasted with that of the nickel hydroxide electrode.



## ELECTROCHEMICA ACTA (Cont.)

2407. Gillibrand, M. I., Wilde, B. E.

9, 401, (1964)

### Thermodynamic Properties of Electrochemical Storage Cells.

The heat evolved when lead/acid electrochemical storage cells are charged and discharged in an adiabatic calorimeter has been determined. The heat-content change and the free-energy change for the reactions which account for the electrical storage capacity of the cell are calculated from the results. These values are the same as have previously been established from emf measurement for the equilibrium reactions in the cell. Similar calorimetric measurements have been made with nickel-cadmium alkaline cells, in which equilibrium conditions cannot be obtained. The heat-content change and the free-energy change for the reactions which account for the electrical capacity of this system are found to be 32.9 Kcal/F and 30.1 KCal/F respectively.

2408. Harivel, J. P., Laurent, J. F.

9, 703, (1964)

### Kinetic Studies of the Decomposition of Active Materials of the Positive Electrode of Nickel Cadmium Alkaline Accumulators.

To compare the several oxidation states obtained during the formation of nickel oxides at different rates of change, and their stability in the presence or absence of foreign ions in their lattice, we have used a method based on the rate of decomposition of these oxides in aqueous media. Measurements have been made based on the time of immersion of an oxidized electrode in a reducing solution. We have shown that the reduction kinetics are first-order, and have deduced rate constants for the reaction at different temperatures as functions of the changing regimes and extents of oxidation. We have calculated the corresponding activation energies.

The stability of the oxides formed during electrochemical oxidation can be estimated from these activation energies. Different results are obtained for pure nickel hydroxide and that containing cobalt.

2409. Appelt, K., Dominiczak, Z., Nowacki, A., Paszkiewicz, M.

10, 617, (1965)

### Electrolytic Production of Nickel Powders and the Employment of them on the Processing of Porous-Sintered Bodies.

The experimental results on the application's possibility of nickel-powder, obtained on the electrolytical way, for the formation of electrodes for fuel cells and active material's skeletons for alkaline storage-batteries, have been presented.

The size-grading, electrolytic precipitates and sinters structure, catalytic properties, over-potential of hydrogen evolution, porosity and sintering conditions of the powder in the temperature of 500 and 700 C has been investigated.

Comparative tests of the powders of other origin (powder obtained from nickel carbonyl and nickel formate) were performed too, in order to determine the differences between their physical and electrochemical properties.



## ELECTROCHIMICA ACTA (Cont.)

The results of the investigations carried out entitle to state, that the light powder obtained electrolytically, may be successfully applied for the sintered electrodes production, instead of commonly used carbonyl nickel powder.

2410. Berndt, D.

10, 1067, (1965)

### The Comparison of Electrochemical Surface Measurements on Porous Electrodes with BET Surface Measurements on Porous Nickel Bodies.

The method of potentiostatic voltage steps was applied to sintered Ni-plates and smooth Ni-electrodes to determine the differential capacity of the electric double layer.

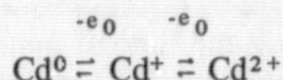
The "electrochemical active surface area" given by this method was found to be in agreement with the BET surface of the sintered plates. The velocity of Hydrogen evaluation at the same electrodes proved to be proportional to the double-layer-capacity too.

2411. Lovreček, B., Marincic, N.

11, 237, (1966)

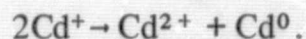
### Kinetics of Electrode Processes of Dissolution and Deposition of Cadmium.

In the mechanism of the multistep electrochemical reaction,



on a stationary drop of Cd-amalgam in  $\text{Cd}^{2+}$  ion solution with and without surface active-agents has been investigated by a galvanostatic method.

In the absence of surfactants, the process appears to be a mixed one, accompanied by  $\text{Cd}^+$ -ion disproportionation,



so that in both the anodic and cathodic directions the first step of the reaction is the slowest ( $n_c^* = 1, n_a^* = 1$ ).

When phenol and gelatin are added the process becomes purely electrochemical. The slowest step in the cathodic direction in this process is then  $n_c^* = 1$ , and in the anodic  $n_a^* = 2$ . This can be explained by supposing that surfactants in cathodic polarization cause partial blocking of the surface by adsorption, whilst in anodic polarization they inhibit the process of disproportionation.



## ELECTROCHIMICA ACTA (Cont.)

2412. Bode, H., Dehmelt, K., Witte, J.

11, 1079, (1966)

### Knowledge of the Nickel Hydroxide Electrode 1. About the Nickel (II) Hydroxyhydrate.

In a series of papers, experimental results leading to a new understanding of reactions and reaction products on the nickel oxide electrode of the alkaline storage battery are reported. The first communication deals with a hitherto unknown compound of bivalent nickel, which is genetically similar to the oxidation products found on a charged nickel oxide electrode.

2413. Brodd, R. J.

11, 1107, (1966)

### Experimental Current Distribution In Porous Battery Electrodes.

The theoretical treatment of Newman and Tobias has been tested using one-dimensional electrode systems. The results are in good qualitative agreement with the theory but suggest that the more complete analysis that includes the effect of back reactions and diffusion should be used if possible. The theoretical relationships confirm the intuitive reasoning of battery engineers, and should serve as a firm basis for future battery electrodes designs. For small values of the reaction parameter  $\delta$  the reaction is uniform, but for large values of  $\delta$  the reaction takes place mainly at the electrode interfaces. Non-uniform reaction distributions result in a lowering of the efficiency of utilization of the active material. The non-uniformity can result from thick electrodes, high current density and poor conductivity of the electrode matrix and/or electrolyte. To insure good utilization of the active material, electrodes should be designed and/or operated with small thickness, low current density and large conductivities of electrode matrix and electrolyte. The results of the report confirm the experimental work of Coleman and of Cahoon and Heise.

2414. Hurlen, T., Sandler, Y. L., Pantier, E. A.

11, 1463, (1966)

### Reactions of Oxygen and Hydrogen Peroxide at Silver Electrodes in Alkaline Solutions.

The intermediate peroxide scheme for the oxygen electrode has been tested by experiments on oxygen reduction and hydrogen peroxide decomposition at silver electrodes in potassium hydroxide solutions (0.1, 1.0 and 5.0 M) at 25 degrees C. The scheme is found appropriate in interpreting the observations, and data are obtained for the specific rate of three of the four one-electron steps involved in the reduction of oxygen to water. The decomposition of hydrogen peroxide occurs at a diffusion-limited rate and gives a mixed potential,  $V(nhe) = 0.94 - 0.059 \text{ pH}$ , when the peroxide concentration exceeds a low limit ( $10^{-6} \text{ M}$  in 1 M KOH). The silver-dissolution reaction exhibits essentially pure diffusion polarization and with the oxygen-reduction reaction determines the open-circuit potential of silver when the peroxide content of the solution is low. The results are compared with previous data on silver and on other electrode materials.



## ELECTROCHIMICA ACTA (Cont.)

2415. Davis, R. E., Horvath, G. L., Tobias, C. W.

12, 287, (1967)

### The Solubility and Diffusion Coefficient of Oxygen in Potassium Hydroxide Solutions.

The solubility of oxygen in aqueous KOH solutions has been measured by a Van Slyke apparatus and by an adsorption technique developed by Hildebrand. In the range of concentration of KOH between 0 and 12 N, at 25 degrees C, the two methods yielded identical results; at 760 torr oxygen partial pressure,

$$\log S = \log 1.26 \times 10^{-2} - 0.1746 C,$$

where 0.1746 is the solubility coefficient,  $S$  the concentration of oxygen, g-mol/l, and  $C$  the concentration of KOH, g-mol/l. Between 0 degrees and 60 degrees C both the solubility and the solubility coefficient decrease with increasing temperature.

Diffusion coefficients of oxygen in aqueous KOH were evaluated from the limiting current of oxygen on a rotating disk electrode, and also by a stagnant tube technique similar to that used by von Stackelberg. The diffusivity drops sharply with increasing KOH concentration, and increases with temperature. At 25 degrees C and for KOH concentrations between 2 and 4 N, the product of the diffusivity and the viscosity is constant:

$$D\mu = 1.3 \times 10^{-7} \text{ g.cm/s}^2,$$

where  $D$  is the diffusivity,  $\text{cm}^2/\text{s}$ , and  $\mu$  is the viscosity in poise. At 60 degrees C and for  $1 < N \text{ KOH} < 8$ , the value of this product is

$$D\mu = 1.9 \times 10^{-7} \text{ g.cm/s}^2.$$

2416. Breiter, M. W.

12, 679, (1967)

### Effect of Scraping on the Anodic Oxidation of Cadmium in Alkaline Solutions.

Voltammetric current/potential curves were measured at 3 and 30 mV/s on smooth Cd electrodes in 1 N KOH with and without scraping of the electrode surface. The effectiveness of the scraping was judged on the basis of results obtained by voltammetry with superimposed ac current. It was found to vary with potential at constant speed of rotation of the electrode and constant force exerted by the scraper against the surface in the region where layers of hydroxide or oxide exist on cadmium. The film that is formed between 0.02 and 0.15 V during the anodic sweep is more stable with respect to scraping than the film produced at more positive potentials. The rate of film removal by scraping is comparable to that of film formation at 3000 rpm during the cathodic sweep between 0.7 and 0.02 V. Film formation occurs on a fresh surface under these conditions.

2417. Bode, H., and Oliapuram, A.

13, 71, (1968)

### Electrochemical Potential of Zinc Crystals in Aqueous Electrolytes.

The potential difference between the different surfaces of zinc single crystals, reported in the literature by several authors, could result either from the formation of different  $\text{Zn(OH)}_2$



## ELECTROCHIMICA ACTA (Cont.)

modifications on the surfaces or from mixed potentials. Careful measurements on clean untreated surfaces exhibited no potential differences at first. A difference in potential is seen after about 20 s, due probably to the formation of different zinc hydroxides. Since mixed potentials are poorly reproducible and dependent on the surface conditions, they could lead to the observation of apparent potential differences between crystal surfaces.

2418. Devanathan, M. A. V. and Lakshmanon, S.

13, 667, (1968)

### Mechanism and Kinetics of Passivation of Cadmium and Zinc in Alkaline Solutions.

The passivation of cadmium and cadmium amalgam in alkaline solutions has been studied by the galvanostatic transient technique. The dependence of  $it^{1/2}$  on  $i$  at low current densities and constancy at high current densities observed fits well with the theoretical relationship derived by Reddy, Devanathan and Bockris. The results are analysed with reference to the dissolution-precipitation mechanism in which the passivating step is the formation of an electronically conducting monolayer of oxide. A mechanism for the passivation of cadmium is proposed, the active intermediate being  $\text{CdOH}^+$  ion. The results of Kaesche have been interpreted to show that a similar mechanism holds good for the passivation of zinc, the probable intermediate species being  $\text{ZnOH}^+$  ion. The recent criticisms by Fleischmann *et al.* of the dissolution-precipitation model based on potentiostatic experiments are shown to be unfounded.

2419. Naybour, R. D.

13, 763, (1968)

### Morphologies of Zinc Electrodeposited from Zinc-Saturated Aqueous Alkaline Solution.

The deposit morphologies produced during the deposition of zinc from an aqueous solution of potassium hydroxide saturated with zinc oxide have been examined by scanning and transmission electron microscopy. Single crystal substrates of orientations (0001),  $(\bar{1}2\bar{1}0)$ ,  $(\bar{1}100)$  and  $(\bar{2}3\bar{1}1)$  were used. The cd was maintained constant in the range 4–100 mA/cm<sup>2</sup>. The deposit morphologies were found to vary with cd; at 100 mA/cm<sup>2</sup> the deposits were dendritic; at 20 mA/cm<sup>2</sup> they consisted of layer growths with some granular growths; at 4 mA/cm<sup>2</sup> they were mossy growths at a density of 10<sup>3</sup>/cm<sup>2</sup>. The principal effect of substrate orientation was the lower the density (10<sup>6</sup> cm<sup>2</sup> compared with 10<sup>8</sup>/cm<sup>2</sup>) of small growths on the basal plane during the early stages of dendritic growth. The density of dendrites after greater passage of charge was found to be independent of the number of small growths and was about the same ( $\sim 10^6$ /cm<sup>2</sup>) for all substrate orientations.

Examination of dendrites by transmission electron microscopy showed that they were monocrystalline with the stem and side branches growing in the  $\langle \bar{1}2\bar{1}0 \rangle$  directions. No evidence for twinning within dendrites was found. The mossy deposits were found to consist of large numbers of small zinc crystals.



## ELECTROCHIMICA ACTA (Cont.)

2420. Appelt, K. and Paszkiewicz, M.

13, 843, (1968)

### Electrolytic Production of Nickel Powder: Influence of Electrolysis Parameters on the Quality of the End Product.

The electrolytic production of fine grained nickel particles in which the run was made with continued electrolysis, is described. The influence of the electrolysis conditions (current, temperature, and  $\text{Ni}^{++}$  concentration) were investigated. The current and the  $\text{Ni}^{++}$  concentration strongly influenced the large grains and the yield. By proper control of the electrolysis conditions, it is possible to attain the desired grain size with a maximum yield of 30-50%.

2421. Yohe, C. D., Riga, A., Greef, R. et al.

13, 1351, (1968)

### Electrochemical Properties of Nickel Oxide.

The electrochemical properties of lithiated nickel oxide in the form of mosaic crystals have been examined. Linear sweep voltammetry of this oxide in  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HClO}_4$ , and  $\text{NaOH}$  reveals a reversible peak at 0.9 V(he), which corresponds closely in potential to that assigned by Pourbaix to the  $\text{Ni(II)/Ni(III)}$  oxide couple. In  $\text{H}_2\text{SO}_4$  a second peak is evident at 1.4 V which corresponds closely to the potential for the  $\text{Ni(III)/Ni(IV)}$  couple. Dissolution rates have been studied in  $\text{HCl}$  at elevated temperatures and found to be surprisingly small. A step-like increment in dissolution rate occurs at potentials corresponding to the first peak (0.9 V) in the voltammetry curves.

Various redox couples have been examined on the lithiated  $\text{NiO}$  crystals. In all instances, the cathodic process is inhibited relative to the anodic process. Tafel linearity has been found for the oxidation of ferrous and ferrocyanide ions after correction for mass-transport control, but the Tafel slopes vary from electrode to electrode at constant lithium content and tend to be lower at low rotation rates. Oxygen reduction to the peroxide is also substantially inhibited as compared with the reverse process. The relative inhibition of cathodic processes is as would be expected generally for a p-type semiconductor.

2422. Takehara, Z., Namba, Y., and Yoshizama, S.

13, 1395, (1968)

### Anodic Oxidation of Silver in Alkaline Solution.

A silver electrode prepared by electrolytic deposition on a platinum wire was oxidized anodically in alkaline solution at constant cd. The impedance change and the potential change after opening the circuit in the course of anodic oxidation were observed and analysed. In the anodic oxidation, crystalline  $\text{Ag}_2\text{O}$  was formed during the first step and then a potential peak appeared; crystalline  $\text{AgO}$  was formed during the second step. The impedance increased exponentially in the course of anodic oxidation and then decreased gradually with the formation of  $\text{AgO}$ , resulting in a maximum impedance. The potential decay after opening of the circuit consisted of a rapid change of ms order and a successive slow change of s order. From these results



## ELECTROCHIMICA ACTA (Cont.)

the rate-determining step in the oxidation process is considered to be the diffusion process of  $\text{Ag}^+$  and/or  $\text{O}^{2-}$  in the oxide layer during the first step, and the crystallization process of  $\text{AgO}$  on the oxide surface during the second step.

2423. Breiter, M. W., and Vedder, W.

13, 1405, (1968)

### Spectroscopic Studies of the Anodic Semiconducting Films on Cadmium Electrodes.

Anodic films were formed on smooth chemipolished Cd electrodes in alkaline electrolytes (0.1-5 M KOH) at constant electrode potential by stepping rapidly from -0.7 to different potentials between 0.03 and 1.0 V referred to a hydrogen electrode in the same solution. The film formation was followed by measuring the current as a function of time. Spectra of the films on the electrode were recorded after the electrodes were removed from the solution as a function of time and potential. The intensity of characteristic bands in the ir region gives an estimation of the amount of  $\text{Cd}(\text{OH})_2$  in the film. If the film is formed in the vicinity of the thermodynamic potential for  $\text{Cd}(\text{OH})_2$  formation, it contains a substantial amount of  $\text{Cd}(\text{OH})_2$ . The  $\text{Cd}(\text{OH})_2$  formation decreases with increase of anodic polarization under the above conditions. Uv spectra of the same films appear characteristic for cadmium oxide and may be a function of the electronic conductivity of the films.

2424. Euler, K. J.

13, 1533, (1968)

### The Change in the Current Distribution in Porous Positive Electrodes of Accumulators and Galvanic Primary Cells During Charge and Discharge.

In the porous thick electrodes of primary and secondary galvanic cells, the distribution of current undergoes characteristic changes during charge and discharge. In general, the current distribution may become more and more even, if the electrode reaction takes place in a homogeneous phase, and if the necessary voltage profile can be developed within the electrode. This is the case with the manganese dioxide electrodes of dry cells. In these electrodes, the current distribution is already evened out after a period representing not more than about 15% of the total cell capacity.

However, the reduction of  $\text{PbO}_2$  and  $\text{NiOOH}$  in lead-acid and in alkaline secondary cells respectively, and of the  $\text{HgO}$  electrode in alkaline primary cells, proceeds in a heterogeneous phase system. Consequently, the initial distribution of current in these electrodes is maintained over a prolonged period. Instead of the evening out of current, here a reaction layer may be observed, moving inwards from the solution electrode interface.

The electrodes discussed are examined by means of electrical analogues. Special attention is paid to the influence of diffusion.



## ELECTROCHIMICA ACTA (Cont.)

2425. Appelt, K.

13, 1727, (1968)

### Concerning the Surface Conductivity of Lead Powders, Cadmium and Nickel Hydroxides (in terms of their lattice structure and electrochemical quality).

Collected results of measurements of surface conductivity of lead oxides, cadmium hydroxides and nickel hydroxides are presented. The advantages of using the method of surface conductivity measurements are discussed. Dependence of surface conductivity on lattice structure is reported. Measurements of surface conductivity along with other methods (X-ray, ir adsorption) may be helpful in investigation of mechanisms of electrocatalytical reactions in porous electrodes. Thus for example an attempt is made to elucidate the electrochemical reduction of  $\text{Cd}(\text{OH})_2$ .

2426. Stonehart, P.

13, 1789, (1968)

### Potentiodynamic Determination of Electrode Kinetics for Chemisorbed Reactants: The $\text{Ag}/\text{Ag}_2\text{O}/\text{OH}$ System.

An examination of current/time (or current/potential) parameters obtained under potentiodynamic conduction is made for adsorbed reactants where a reverse reaction and diffusion of the products are of no consequence. Particular attention has been paid to the implications of varying reaction orders for the electrode reactions. The equations have been used to examine in detail the formation (second-order) and reduction (first-order) of  $\text{Ag}_2\text{O}$  in 1 N NaOH. The silver electrodes were prepared as thin films on rhodium substrates to control the mass of reacting silver. The transfer coefficient was determined from experimental results for both formation and reduction of  $\text{Ag}_2\text{O}$  to be  $\alpha = 0.71 \pm 0.03$ . The formation of  $\text{AgOH}$  is rapid and is distinguished from the formation of  $\text{Ag}_2\text{O}$  so that different values of the standard electrode potential for the  $\text{Ag}/\text{AgOH}/\text{OH}^-$  and the  $\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-$  couples can be determined. The  $\text{Ag}/\text{AgOH}/\text{OH}^-$  couple is considered to be the potential-determining reaction for the reversible silver/silver-oxide electrode.

2427. Stonehart, P., and Portante, F. R.

13, 1805, (1968)

### Potentiodynamic Examination of Surface Processes and Kinetics for the $\text{Ag}_2\text{O}/\text{AgO}/\text{OH}$ System.

A detailed examination of the  $\text{Ag}_2\text{O}/\text{AgO}/\text{OH}^-$  system with linear potentiodynamic and trapezoidal potentiodynamic control of the electrode potential shows a non-stoichiometry for  $\text{AgO}$  formation with approximately 1 in 6 silver atoms in the  $\text{Ag}(\text{III})$  state. An autocatalytic reaction accounts for the formation of  $\text{AgO}$  from  $\text{Ag}_2\text{O}$  at constant potential, provided that the reaction is initiated by electrochemical production of a number of  $\text{AgO}$  sites. Reduction of  $\text{AgO}$  is a first-order reaction with a specific rate constant  $k = 3.2 + 0.9 \times 10^{-3} \text{ s}^{-1}$ , and a transfer coefficient  $\alpha = 0.55$ . The reduction mechanism is  $\text{Ag}^{3+} + 2\text{e}^- \rightarrow \text{Ag}^+$  and is in agreement with results obtained using steady state conditions.



## ELECTROCHIMICA ACTA (Cont.)

2428. Vogel, W. M.

13, 1815, (1968)

### Electrochemical Evidence for High Valency States of Nickel.

Evidence is presented which indicates the existence, in hot concentrated potassium hydroxide (85 wt-% KOH), of reversible homogeneous nickel redox couples in which nickel exhibits valencies greater than two. Coarsely crystalline nickel oxides in which the nickel apparently has valencies as high as 3.6 have been prepared and isolated as shiny black crystals.

2429. Jolas, F.

13, 2207, (1968)

### Zinc Electrodes in Alkaline Media.

The various theories on the behaviour of zinc in alkaline solutions, and some aspects of actual problems arising from the manufacturing of alkaline cells using a zinc electrode, are analysed.

The thermodynamic constants and the conditions of formation of zinc oxides and hydroxides existing in alkaline medium are given. The dissolved species of zinc in alkaline solutions are considered and the relation between electrode potential, activities of dissolved species and pH is given.

Anodic and cathodic behaviour of the zinc electrode is discussed, special attention being drawn to dissolution in the active state and to passivation phenomena. The conditions of formation and the nature of passive anode layers are described.

Problems arising from utilization of zinc electrodes in primary and secondary alkaline cells are presented. Means to defer anodic passivation are discussed and the mechanism of dendrite formation during cathodic polarization is analysed. Possible interferences between positive and negative electrodes are also noted.

2430. Harivel, J. P., and Laurent, J. F.

13, 2229, (1968)

### Iron and Cadmium Electrodes from Alkaline Accumulators.

A short summary is given of the development and use of cadmium and iron electrodes in alkaline secondary batteries.

2431. Kramer, G.

13, 2237, (1968)

### The Negative Electrode in Gas-Tight Alkaline Accumulators.

Hermetically closed alkaline secondary batteries depend on the precisely correct dimensions of the electrodes, and on excluding absolutely the evolution of hydrogen under all practical conditions. Whereas safety requirements against polarity reversal are limited to special cases, breakdown-free functioning must be absolutely guaranteed during overcharge, during normal use and during standby periods. To assure this, the negative electrode must be equipped with a suitable active mass and must have a matched capacity, divided properly into charge reserve, utilizable capacity and discharge reserve. The capacity repartition correlates closely with the charge condition at the moment when the cell is hermetically closed.



## ELECTROCHEMISCHE, ZEITSCHRIFT FÜR

2500. Le Blanc, M., and Müller, R.

39, 204, (1933)

### Contribution to the Knowledge of the Nickel Oxide Oxygen-Water System.

Through the experiments of Le Blanc and Sachse, it has been proven that the dry process yields no definite higher nickel oxides. While the yellow green NiO may accept the oxygen in the active form with black coloration and increased efficiency, the fine structure remains unchanged as the x-rays indicate. It is now of interest to determine if perhaps a higher defined nickel oxide could exist in the presence of water.

2501. Georgi, K.

39, 209, (1933)

### Concerning the Anodic Behavior of Cobalt.

The previously published work on the anodic behavior of nickel had shown the distinct dependence of the resistance of the  $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$  process on the type of anion. The potential required for the equal rapidity of the nickel formation shows it to be much larger the larger the anion. It could be expected that the influence of the anion size would also be exerted in the anodic process on other metals which are electrochemically soluble, especially those from the iron group. Closest to nickel in regard to electrochemical behavior, is cobalt (according to the work of Schildback and especially Byers and Thing.)

2502. Le Blanc, M., and Mobius, E.

39, 753, (1933)

### X-Ray Studies of the Nickel-Oxygen-Water System (Remarks on the Treatise by R. W. Cairns and E. Ott).

A short time ago Le Blanc and Müller summarized the results of their investigation on the Nickel Oxide-Oxygen-Water System in the following sentences: "During the isothermal reduction of the higher nickel oxides containing water, neither constant oxygen nor water vapor pressures were found. This result speaks against the existence of chemically defined higher oxides and hydrates of nickel." The Debeye-Scherer patterns of samples prepared at  $0^\circ$  show interference patterns which are so unclear and blurred that one cannot give an opinion on identifying the crystal structure.

2503. Grube, G., and Vogt, A.

44, 353, (1938)

### The Time Dependent Processes of Polarization of the Nickel Anode During the Electrolysis of Water in Alkaline Solutions.

It is known that by the use of nickel anodes and iron cathodes in the electrolysis of water in alkaline solution, the overpotential due to gas evolution at constant current increases with time. Consequently, the voltage across the terminals also increases steadily in a freshly initiated electrolysis.



## ELECTROCHEMISCHE, ZEITSCHRIFT FÜR (Cont.)

2504. Glemser, O., Einerhand, J.

54, 302, (1950)

### The Chemical Processes on the Nickel Hydroxide Anode of the Edison Battery.

The reaction mechanism in the Edison battery is newly formulated as



Ni(OH)<sub>2</sub> and NiOOH (B-NiOOH) crystallize in the C 6 type; B-NiOOH has Arnfelt structure, Ni(OH)<sub>2</sub> has "roughened crystal-lattice planes" and flake-shaped formation of the crystallites. The charging process is not the reverse of the discharging process. In charging, NiO<sub>2</sub> · xH<sub>2</sub>O occurs as primary product from which B-NiOOH develops by disintegration or reaction with Ni(OH)<sub>2</sub>. With properly conducted discharge, Ni<sub>3</sub>I<sub>2</sub>(OH)<sub>4</sub> manifests itself by a potential stage. Ni<sub>3</sub>O<sub>2</sub>(OH)<sub>4</sub> can be produced by the reaction 2 NiOOH + Ni(OH)<sub>2</sub> = Ni<sub>3</sub>O<sub>2</sub>(OH)<sub>4</sub>, or it can be formed by decomposition from B-NiOOH. If the Edison battery stands for a long time, the decomposition from B-NiOOH to Ni<sub>3</sub>O<sub>2</sub>(OH)<sub>4</sub> must effect a decrease in capacity.

2505. Huber, K.

62, 675, (1958)

### The Structure of Passivating Layers.

According to a list of the points of view which are decisive for the evaluation of passivating layers, it is shown that:

1. On one and the same metal (Zn), covering layers in which the crystalline portion is always the same (ZnO), can have quite different structures depending on formation conditions and are only inadequately described with the model of a plane-parallel plate.
2. The same structure (that of "eloxal" layers) occurs in anode covering layers in systems which are chemically completely different. Reference is made to the form of this structure.
3. Primary anode oxide layers (MgO, CdO, Al<sub>2</sub>O<sub>3</sub>) can be changed by reaction with the electrolyte, thus producing structures of a peculiar type.

2506. Ohse, R. W.

64, 1171, (1960)

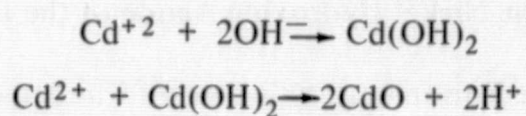
### An Oscillographic Investigation of Electrode Reactions in the Cd/Aqueous Solution System with the Intermittent Galvanostatic Measuring Electrode.

The electrode reaction which occurs during the electrical loading of Cadmium in Aqueous Solutions was investigated by means of an intermittent galvanostatic method using oscillographic recording of the voltage/time curves. During the anodic loading with specific current densities, two voltage levels below the equilibrium delivered voltage of the oxygen electrode were observed. The quiescent delivered voltages which were measured during intermittent loading were found to



## ELECTROCHEMISCHE, ZEITSCHRIFT FÜR (Cont.)

be caused by the production of  $\text{Cd}(\text{OH})_2$  and  $\text{CdO}$  according to the electrode reactions,



The thusly demonstrated time sequence of the electrode reactions which lead first to be production of  $\text{Cd}(\text{OH})_2$ , and then  $\text{CdO}$ , were compared with the structural investigations elsewhere which showed a layering of localized sequence  $\text{Cd}/\text{CdO}/\text{Cd}(\text{OH})_2/\text{OH}^-$  solution. Besides these findings, the oscillographic measurements produced indications of the production of a higher cadmium oxide and cadmium hydride. The reaction mechanism with cathodic leading was considered by measuring the level of charge and the influence of oxygen.



## FARADAY SOCIETY, DISCUSSIONS

2600. Roberts, M. W., Wells, B. R.

62, 162, (1966)

### Nature and Reactivity of Nickel and Oxidized Nickel Surfaces.

The role of oxygen in determining the surface characteristics of nickel catalysts has been investigated by work function, photoelectric and chemical reactivity studies. The possible limitations of any one particular method are discussed. Surfaces which have been exposed to oxygen ( $10^{-4}$  mm min) at 23 degrees exhibit the characteristics expected of a surface oxide although the chemical reactivity is not that associated with NiO. Oxide structures of low work function can form, and these were shown to have specific adsorption characteristics.

The adsorption of carbon monoxide and oxygen and the catalytic oxidation of carbon monoxide by heavily oxidized nickel films were studied. Two distinct states of adsorbed oxygen were recognized. A substantial decrease in work function occurred on adsorbing carbon monoxide, the decrease being greater the higher the temperature. At 170 degrees and 1.5 mm the decrease was  $\sim 0.85$  eV, the major portion of this arising from a space charge term. The oxide work function remained virtually unchanged during catalysis at 23 degrees. This was due to a low energy state of adsorbed oxygen inhibiting the adsorption of carbon monoxide thereby preventing the development of a space-charge.



## FARADAY SOCIETY, TRANSACTIONS

2700. Hickling, A., Spice, J. E.

43, 762, (1947)

### The Anodic Behavior of Metals. Part III—Nickel.

In Parts I and II, the anodic polarization of the noble metals platinum and gold was investigated by an oscillographic method which records the variation of potential with quantity of electricity passed prior to oxygen evolution. The method has now been applied to nickel which was selected as a metal which readily becomes passive. No previous work on nickel from the present standpoint has been published, but a certain amount of information on the anodic behaviour of the metal is available from other methods of investigation. The general conclusion reached from numerous passivity studies is that nickel in the passive state is covered with a protective film, probably of nickelic oxide  $\text{Ni}_2\text{O}_3$  or hydroxide  $\text{Ni}(\text{OH})_3$ .

2701. Briggs, G. W. D., Jones, E., Wynne-Jones, W. F. K.

51, 1433, (1955)

### The Nickle Oxide Electrode, Part I.

The preparation of Ni oxide electrodes suitable for quantitative work is discussed and methods for preparing Ni oxide layers in  $\text{NaClO}$  solution and by electrodeposition are described. Polarization curves for both types of electrode at constant current in  $\text{KOH}$  solution are discussed and it is shown that the coulombic efficiency of the electrode reaction may approach 100% in suitable conditions. Results are discussed with brief reference to the changes in composition of the oxide layer during charging and discharging.

2702. Jones, E., Wynne-Jones, W. F. K.

52, 1260, (1956)

### The Nickel Oxide Electrode, Part II.

A detailed account is given of the electrochemical behavior of nickel oxide electrodes prepared by methods described in a preceding paper. Potential against time and potential against composition curves are discussed for conditions existing both on open circuit and during the passage of current. Methods for chemical analysis of the oxide layers are described, and it is shown that the existence of variations in composition within the oxide layer may account for many features of the electrode phenomena. A possible mechanism whereby such variations may be set up is indicated.

2703. Briggs, G. W. D., Wynne-Jones, W. F. K.

52, 1272, (1956)

### The Nickel Oxide Electrode, Part III.

X-ray powder patterns of deposits from nickel oxide electrodes have been obtained to supplement chemical analysis. The compounds present at different stages of charging and dis-



## FARADAY SOCIETY, TRANSACTIONS (Cont.)

charging of freshly prepared  $\text{Ni(OH)}_2$  electrodes have been identified and the presence of two distinct stages in the electrode process has been confirmed. By means of X-ray data and measurements of electrochemical capacity it is shown that aged  $\text{Ni(OH)}_2$  is difficult to oxidize electrolytically and that  $\text{NiO}$  apparently undergoes only a surface reaction. The diffraction evidence is discussed in relation to the electrochemical behavior of each class of electrode.

2704. Devanathan, M. A. V., Selvaratnam, M.

56, 1820, (1960)

### Mechanism of the Hydrogen-Evolution Reaction on Nickel in Alkaline Solutions By The Determination of the Degree of Coverage.

The coverage of nickel cathodes with adsorbed atomic hydrogen in 2 N alkaline solutions has been determined by the double-charging method of Devanathan, Bockris and Mehl. Values are reported for various anodic c.d.s. ranging from  $0.05 \text{ A cm}^{-2}$  to  $1.8 \text{ A cm}^{-2}$  at a constant cathodic c.d. of  $10^{-4}$ . The results show that re-adsorption is negligible at c.d.'s greater than  $0.6 \text{ A cm}^{-2}$ . The variation of adsorbed hydrogen over cathodic c.d.'s ranging from  $10^{-6}$  to  $10^{-1}$  at a constant anodic c.d. of  $1 \text{ A cm}^{-2}$  are given and the coverage  $\theta$  calculated. The mechanism of the hydrogen-evolution reaction has been elucidated using these values of  $\theta$ . It is shown that the rate-determining process is slow discharge from a water molecule and that this is followed by a rapid Tafel recombination. The rate constants for these processes have been evaluated. It is shown that the classical Tafel equation and other modifications of it are not satisfactory. A new equation involving a different  $i_0$  value for the ionization current is suggested. Calculations based on this equation show that when allowance is made for the ionization current and coverage a linear Tafel plot is obtained at all c.d.'s. It is suggested that determination of Tafel constants are best made after making allowance for ionization and coverage.

2705. Conway, B. E., Bourgault, P. L.

58, 593, (1962)

### Significance of E. M. F. Decay Measurements. Applications to the Nickel Oxide Electrode.

The significance of observations of rates of e.m.f.-decay on open-circuit at the nickel oxide electrode is examined in terms of the potential dependence of the surface capacitance associated with the process occurring during decay. Results are compared with those reported by Lukovtsev and Temerin and it is concluded that a capacity based on the properties of the surface layer (e.g., adsorbed oxygen radicals or a highly oxidized nickel oxide surface phase) must be used rather than one based on the oxidation-reduction behavior of the bulk phase oxide. Direct micro-volumetric determinations of volumes of oxygen evolved from the electrode during open-circuit e.m.f.-decay allow quantitative comparisons to be made between true Tafel slopes and open-circuit e.m.f.-decay slopes. These slopes are shown to be identical only when the volume of oxygen evolved from the surface is a linear function of e.m.f. When the e.m.f. is a logarithmic function of the oxygen evolved, Tafel and decay slopes are shown to differ in the theoretically expected direction. The linear and logarithmic behavior with respect to e.m.f. and volumes of oxygen evolved can be shown to follow as limiting conditions of the adsorption behavior of oxygen at the electrode surface, depending upon the extent of surface coverage. The kinetic significance of the surface capacitance is discussed in relation to the e.m.f. decay behavior.



FARADAY SOCIETY, TRANSACTIONS (Cont.)

2706. Fleischmann, M., Rajagopalan, K. S., Thirsk, H. R. 59, 741, (1963)

Kinetics of Electrocrystallization of Thin Films of Cadmium Hydroxide.

The formation of cadmium hydroxide on cadmium amalgam has been examined in alkaline solutions at constant potential. Approximately three monomolecular layers are deposited before passivation with the basal plane of the hexagonal crystals parallel to the amalgam. The kinetics of formation of the first two layers are analyzed. It is shown that the slow stage of crystal growth is the formation of the lattice at the periphery of two-dimensional growth centres of monomolecular height, randomly nucleated on the surface. The variation of the crystal growth constant with potential and concentration implies that the rate-determining step is a rearrangement of two adsorbed hydroxide ions into the lattice planes containing these ions.

2707. Farr, J. P. G. and Hampson, N. A. 62, 3493, (1966)

Reactions at Solid Metal Electrodes Part 1.  
Faradaic Impedance of Zinc Electrodes in Alkaline Solution.

The results of impedance measurements at zinc electrodes in alkali are presented. The effects of adsorption at these electrodes are discussed and it is shown that zinc electrodes of different metallurgical histories display corresponding differences in reactivity.

2708. Brieter, M. W., Vedder, W. 63, 1042, (1967)

Nature of Anodic Films on Cadmium in Alkaline Electrolytes.

Smooth cadmium electrodes with a surface essentially free of cadmium oxide and hydroxide were oxidized at constant potential between 0.05 and 1.0 V in various alkaline electrolytes. Layer formation was followed by recording the current as a function of time. Anodic films formed after different oxidation times at various potentials were investigated by electron microscopy, infra-red spectroscopy, and X-ray diffraction. The films grow nonuniformly on the surface. The number of nuclei increases with oxidation potential. Infra-red spectra demonstrate the presence of  $\beta$ -Cd(OH)<sub>2</sub> or  $\gamma$ -Cd(OH)<sub>2</sub>, or a mixture of both types of hydroxide in agreement with the X-ray diffraction results. The total amount of hydroxide decreases with potential and is, in general, smaller than the amount corresponding to 100% efficiency of hydroxide formation. This deficit is attributed to the simultaneous formation of amorphous CdO. During the reduction at constant cathodic potential cadmium oxide and  $\gamma$ -Cd(OH)<sub>2</sub> disappear first, and then  $\beta$ -Cd(OH)<sub>2</sub>. The conversion of anodically formed CdO into  $\beta$ -Cd(OH)<sub>2</sub> is a slow process.



FARADAY SOCIETY, TRANSACTIONS (Cont.)

2709. Briggs, G. W. D., Fleischmann, M., et al.

64, 3120, (1968)

Texture, Growth and Orientation of Anodically Formed Silver Oxides.

The structure, topography and growth of silver oxide deposits formed under galvanostatic and potentiostatic conditions in potassium hydroxide solutions has been studied by X-ray and electron diffraction and by electron microscopy. The argentous oxide deposit cannot be classified as being either continuous or discontinuous, but has features associated with both types of film. A random deposit is formed initially followed by the development of one-degree orientation. The argentous oxide film has a marked orientation and a proportion of orientation parallel to the electrode surface. Orientated argentic oxide deposits were not found under any conditions.

2710. Fleischmann, M., Lax, D. J., and Thirsk, H. R.

64, 3137, (1968)

Electrochemical Studies of the  $\text{Ag}_2\text{O}/\text{AgO}$  Phase Change in Alkaline Solutions.

The anodic oxidation of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$  in potassium hydroxide solution has been investigated by controlled potential oxidations at  $25^\circ\text{C}$ . Separate  $\text{Ag}/\text{Ag}_2\text{O}$  electrodes of fixed electrochemical capacity were oxidized at controlled potential using steps of 20 mV over a range of 300 mV and the corresponding current-time curves were recorded. By correlating the structure of the deposit with the kinetic studies the growth geometry and nucleation law for the oxidation of  $\text{Ag}_2\text{O}$  deposits in alkaline solutions were determined. The oxidation of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$  involves the progressive nucleation of  $\text{AgO}$  centres coupled with three-dimensional growth. A mechanism for lattice formation is proposed based on the concentration and potential dependence of the rate of crystal growth.



## GERMAN ELECTROTECHNOLOGY (DEUTSCHE ELEKTROTECHNIK)

2800. Winkler, H.

12, 531, (1957)

### Concerning Investigations of the Reactions in Gastight Ni-Cd Accumulators.

Recently, alongside nickel-cadmium accumulators of customary construction, there are also being produced so-called gas-tight, hermetically sealed nickel-cadmium accumulators, which require practically no attendance. The discharge voltage of gas-tight accumulators is not distinguishable from that of normal accumulators; on the other hand, the course of the charging voltage is distinguishable. The charging voltage of gas-tight accumulators gradually increases to a constant value; contrariwise, the normal nickel-cadmium accumulator exhibits a characteristic voltage rise. By measuring the single electrode potentials against zinc it can be demonstrated that the high voltage rise is caused by the cadmium electrode. It was assumed that the voltage rise is related to the evolution of gas at the electrodes.



INDIAN ACADEMY OF SCIENCES, PROCEEDINGS OF THE

2900. Sanghi, I., Fleischmann, M.

Sec. A, 49, 6, (1959)

Electrochemical Behavior of Zinc in Alkaline Solutions Part II.  
Constant Over-Voltage Measurements.

As the whole passivation phenomenon in the case of zinc is very quick and sudden and as it cannot be fully studied and followed by galvanostatic techniques alone, the constant over-potential technique has, for the first time, been applied to zinc and results reported. A special apparatus consisting of suitable oscillator, modulator, demodulator and a stable D.C. amplifier with a gain of 100,000 was used for the purposes and is described. Potential curves for equilibrium current rates, achieved in 0.1 V. and 25 mV. steps after 1 minute each, have been obtained in 6 N, N, 0.1 N KOH and zincate solutions for the complete range of  $-1.3$  to about  $-2.0$  volts with reference to Hg/HgO/KOH reference electrode. It has been found that in the first truly active region, the main electrode reaction is the formation of zinc ions while after the passivation it changes to gas evolution. Potentiostatic techniques, reveal intermediary stages, undisclosed by constant current methods, of pseudo-passivation and current-plateau regions in which the anodic layer thickens, controlled by the high field cation transport. These observations and explanations are further supported by plotting rate-time transients obtained by suddenly dropping the potentials from higher to lower values, when the rates were found to cut off. Some anomalies and sudden reversal of currents with increasing over-voltages, have also been fully discussed.



## INDUSTRIAL AND ENGINEERING CHEMISTRY

3000. Tichenor, R. L.

44, 973, (1952)

### Nickel Oxides-Relation between Electrochemical Reactivity and Foreign Ion Content.

The marked electrochemical effects of adding lithium, bismuth, and iron to the nickel electrode of alkaline storage batteries have been known for many years. Heretofore, no adequate explanation of how additions of these metals affect the electrode has been published. The theory given in this paper explains these effects using the following postulates: Electrolytic oxidation and reduction of nickel oxide are terminated by creation of insulating barrier layers of nickel oxide adjacent to the electronic conductor. "Foreign" ions such as those of lithium, bismuth, and iron enter into the crystal of nickel oxide by substitution, replacing nickel ions. The presence of these foreign ions affects the stability of the oxidation states of adjacent nickel ions. This change in stability retards or promotes oxidation of the nickel oxide, it also affects the growth of the insulating barrier layers. Both factors may affect the extent to which the oxide can be oxidized or reduced.

3001. Newman, J.

60, 12, (April 1968)

### Engineering Design of Electrochemical Systems.

Engineering design procedures for electrochemical systems have not been developed as thoroughly as for mass transfer operations like distillation. Nevertheless, the fundamental laws governing electrochemical systems are known. The purpose of this paper is to review the analysis of certain electrochemical systems in relation to these fundamental laws. To a greater or lesser extent, one is concerned with fluid flow patterns, ohmic potential drop in solutions, restricted rates of mass transfer, and the kinetics of electrode reactions. The situation is complicated as well by the variety of specific chemical systems. These examples provide some of the main tools of the electrochemical engineer.



INORGANIC AND NUCLEAR CHEMISTRY, JOURNAL OF

3100. Dirkse, T. P., Vander Lugt, L. A., Schnyders, H.

25, 859, (1963)

The Reaction of Silver Oxides with KOH.

The dissolution of silver oxides in aqueous potassium hydroxide solutions has been followed by determining solubility and by observing the changes in potential of a silver electrode in such solutions. The effect of solubility with time has been studied and the identity of the black decomposition product has been determined. The extent to which silver oxides dissolve in aqueous potassium hydroxide is determined by several reactions.

3101. Dirkse, T. P., Vander Hart, D., Vriesenga, J.

27, 1779, (1965)

The Decomposition of Silver Oxide in KOH Solutions.

The decomposition of silver(I) oxide in aqueous potassium hydroxide has been studied using titrimetric, radioactive tracer, and gas evolution techniques. The rate of decomposition is dependent on temperature, photo effects, and the presence of foreign materials.



**INTERNATIONAL COMMITTEE OF ELECTROCHEMICAL THERMODYNAMICS  
AND KINETICS (CITCE)**

3200. Winkler, H.

8, 383, (1956)

**The Processes of the Nickel Hydroxide Electrode of Nickel Cadmium Accumulators.**

Glemser and Einerhand have investigated the processes of the nickel hydroxide electrode. They have established that the electrochemical process at the positive electrode during the charge results primarily in the production of  $\text{NiO}_2 \cdot x \text{H}_2\text{O}$ . This product should decompose spontaneously into B-NiOOH or transfer itself together with the nickel hydroxide still present in the mass to B-NiOOH. It can only be reconfirmed by the investigation of Glemser and Einerhand.

3201. Winkler, H.

9, 320, (1957)

**A Contribution to the Processes in Gas-Tight Nickel-Cadmium Accumulators.**

Recently, aside from nickel-cadmium accumulators of the traditional type, there have also been manufactured gas-tight sealed nickel-cadmium accumulators that need practically no maintenance. The discharge voltage of gas-tight accumulators is not different from the normal type; the course of the charging voltage, on the other hand, is different.

3202. Trägårdh, U.

9, 326, (1957)

**The Potential of the Positive Electrode from Alkaline Accumulators and Dependence on Solution Concentration.**

After forming of a newly manufactured nickel electrode with an exactly known quantity of  $\text{Ni(OH)}_2$ , the electrode was charged and discharged several times in alkaline solutions of various concentrations from 0.5 to 10 N at  $18 \pm 1^\circ$ . During the charge, the quantity of electricity used for the oxidation was monitored by means of gas analysis. The potential was evaluated against an HgO reference electrode with a VTVM. The discharge was constant current to 0.0V.

3203. Gerischer, H.

9, 352, (1957)

**The Kinetics of the  $\text{Ag/Ag}^+$  aq Electrode  
(A Contribution to the Question of the Mechanism of Electrocrystallization).**

A procedure is described by which one can separate the activation and resistance polarization in a current-carrying electrode from concentration polarization. In evaluating the results, it is found that electrocrystallization in a silver electrode in an  $\text{AgClO}_4$  solution reacts to form a transition state which is referred to as Ad-atom. The concentration of adsorbed atoms at equilibrium conditions is of the order of magnitude of 2% of atomic layer.



INTERNATIONAL COMMITTEE OF ELECTROCHEMICAL THERMODYNAMICS  
AND KINETICS (CITCE) (Cont.)

3204. Yoshizawa, S., Takehara, Z.

17th Meeting, Sept. (1966)

Electrode Kinetics of Nickel Hydroxide in Alkaline Solutions.

In order to ascertain the charge-discharge reaction mechanisms of the nickel hydroxide electrode and to acquire the rate determining step, electrode kinetics of the nickel hydroxide electrode and effects of  $\text{Li}^+$  ion and rare earth compounds were studied by means of decay and growth of overpotential or polarization.



## INTERNATIONAL JOURNAL OF POWDER METALLURGY

3300. Evans, P. E., Ashall, D. W.

1, 32, (1965)

### Grain Growth in Sintered Nickel Powder.

Grain growth in sintered nickel has been studied in the temperature range 900-1125 C. The average spatial grain diameter  $D$  varies with sintering time  $t$ , at a sintering temperature  $T$  ( $^{\circ}\text{K}$ ) according to the equation

$$D^2 - 4.32 = K_0 t^{0.93} \exp \frac{-29,300}{RT}$$

Spherical pores, present in various concentrations in samples compacted at different pressures, have no detectable effect on the kinetics of grain growth in this material.

3301. Hancock, H. A., Evans-Mackiw, D. J. I.

1, 42, (1965)

### Sintered Plates from Low Density Nickel Powders.

Special low density nickel powders suitable for the production of porous matrices are described with particular reference to nickel-cadmium battery plates. The results of gravity sintering tests are given to show the relationship between the physical characteristics of the powders and their sintering behaviour. The variables investigated include apparent density, Fisher number, particle size, surface area, sintering time and sintering temperature. The plaques made from these powders by gravity sintering were evaluated for porosity, electrical resistivity, shrinkage and strength. Powders with apparent densities as low as 0.5 g/cc gave plaques with up to 90% porosity and very low shrinkage.

3302. Williams N. J., and Tracey, V. A.

4, 47, (1968)

### Porous Nickel for Alkaline Battery and Fuel Cell Electrodes: Production by Roll Compaction Method.

The nickel structure used in nickel-cadmium alkaline battery electrodes must possess high porosity (70-90%), to hold the active mass, have low electrical resistance, to minimize potential gradients, and possess mechanical strength adequate to withstand the stresses encountered during manufacture and service. In the porous nickel employed for fuel cell electrodes the requirements ask for a narrow pore spectrum and a highly-active internal surface. The latter property is generally conferred by an 'activation' treatment, subsequent to the production of the electrode.



INTERNATIONAL JOURNAL OF POWDER METALLURGY (Cont.)

3303. Juusela, J., Rekola, T., et al.

5, 91, (1969)

On the Use of Scanning Electron Microscopy in Powder Metallurgy.

The lack of a suitable optical research instrument has made it difficult to study the structure of powder metallurgical materials. This kind of research has for the present been carried out mainly by using common metallographical technique which has its well known limitations. The inherent porosity of powder metallurgical materials makes the use of the common electron microscope quite limited since the preparation of transmission specimens is extremely difficult, if not impossible.

A couple of years ago a new type of electron microscope, the Scanning Electron Microscope, was put on the market. This instrument is a stereo microscope with high resolution power. It allows sharp three-dimensional vision of the specimen surfaces even in case of rather rough surfaces.

It is the aim of the authors to show with the photographs what can be done with this instrument when studying porous materials.



## INTERNATIONAL POWER SOURCES SYMPOSIUM

The 1962 Symposium Proceedings Published in Batteries, Edited by D. H. Collins, Pergamon Press (1963).

3400. Doran, R. J. 3, 105, (1962)

### The Nickel-Scandium Hydroxide Electrode.

Substantial elevation of the working potentials of the nickel hydroxide electrode and a marked improvement in the reversibility of the electrode result from the incorporation of a moderate percentage of scandium ion in the active material.

The electrode behaviour of nickel-scandium hydroxide is described and compared with that of nickel hydroxide. Its potential usefulness in specialized applications of the nickel-alkaline battery, notably as a storage battery for satellites, is briefly discussed.

3401. Thomas, U. B. 3, 117, (1962)

### Kinetic Basis for the Operating Characteristics of Sealed Ni-Cd Cells.

Some of the kinetic parameters important in determining the capabilities and the limitations of sealed nickel-cadmium storage cells are considered and examples are cited to show how they affect the practical application of such batteries.

The differences in properties between sealed and open cells are discussed in relation to these parameters.

3402. Farmery, H. K., Smith, W. A. 3, 179, (1962)

### Some Material Problems in the Silver-Zinc Secondary Battery.

Whilst the silver-zinc cell is still considered by many to be an expensive and exotic form of potted powder, suitable only for special applications involving a few cycles, considerable progress has been made in the last decade in improving its long-term reliability for use as a secondary battery.

From the fundamental point of view, the sequence and kinetics of the electrode reactions have been the subject of much study. The positive electrode, in particular, has received considerable attention and there is substantial agreement amongst the various workers on the reactions involved, although the possible formation of oxides higher than AgO is still the subject of controversy. Reactions at the negative electrode have been less thoroughly investigated, and much remains to be done in this field.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3403. McKie, A. S., and Clark, D.

3, 285, (1962)

### Crystallographic and Chemical Studies of the Oxides of Silver.

Existing knowledge of the chemistry and crystal structure of the oxides and so-called peroxy-compounds of silver is briefly reviewed.

A tetragonal oxide of empirical formula  $\text{AgO}$  has been prepared by the action of ozonized oxygen on hot silver powder and its structure has been determined; this oxide is distinct from the monoclinic  $\text{AgO}$  commonly found in charged silver electrodes. It contains silver in two kinds of crystallographic position and pairs of oxygen atoms apparently doubly bonded.

The structures of silver peroxy-nitrate  $\text{Ag}_7\text{NO}_{11}$  and peroxy-sulphate  $\text{Ag}_7\text{SO}_{12}$  have been determined: the conclusion is reached that these compounds may have a variable composition but that the formulae given above represent a saturation of the holes in a cubic  $\text{Ag}_6\text{O}_3$  lattice with ions of the salts  $\text{Ag(I)NO}_3$  and  $\text{Ag(II)SO}_4$  respectively.

1964 Symposium Proceedings Published in Batteries II, Edited by D. H. Collins, Pergamon Press (1965).

3404. Salkind, A. J., Bodamer, G. W.

4, 55, (1964)

### Changes in Physical Chemical Properties of Secondary Battery Electrodes During Cycling.

Although research workers in the battery field have long recognized that significant changes occur in physical chemical properties of the active materials during discharge of both primary and secondary batteries, relatively little has been published in the way of actual data obtained during manufacture and subsequent prolonged cycling. It is the authors' aim in this paper to show the utility and limitations of such methods as chemical analysis, X-ray examination, surface area determination, Tafel overvoltage, and porosity measurements in understanding the behavior of battery electrodes. To illustrate the utility of these techniques, we will use data from a five-year cycling program on nickel-cadmium cells now underway in our company. This program is part of a project which was initially partially sponsored by Bell Telephone Laboratories. The program is approximately at its mid-point with about two and a half years of data being reported at this time.

3405. Bagshaw, N. E., Gillebrand, M. I., Wilson, K. P.

4, 81, (1964)

### The Microscopic Examination of Active Materials from Ni-Cd Alkaline Cells.

Since the reactions occurring during the charging and discharging of the nickel-cadmium alkaline cell are not completely understood, it is desirable to collect any further information which may be made available by the use of other experimental methods. Simon and Jones have used microscopic techniques for the investigations of reactions occurring in lead-acid battery electrodes and Briggs and Wynne-Jones have made similar observations on small wire electrodes. It was considered that microscopic observations of battery plates had the advantage that the changes involved substantial amounts of material which would possibly ease the task of identification. Recently, we have obtained colour photomicrographs of the active materials in alkaline battery plates and these observations are the subject of this paper.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3406. Appelt, K.

4, 93, (1964)

### The Effect of Crystal Habit and Surface Properties on the Electrochemical Properties of Porous Electrodes Made of $\text{Cd}(\text{OH})_2$ .

Hard water washing causes a decline in the electrochemical activity of cadmium hydroxide. Close examination showed that this decline is due to adsorption of calcium and magnesium compounds present in the hard tap water on the cadmium hydroxide.

This fact suggested the existence of an interdependence between the structural and surface properties of the active agents of galvanic cells and their electrical capacity. The search after such properties in the case of cadmium hydroxides prepared under different conditions was the aim of the present paper.

3407. Harivel, J. P., Morignat, B., Migeon, J.,

4, 107, (1964)

### Investigations on the Negative Electrode of Ni-Cd Cells with Sintered Plates.

The behaviour of cadmium and zinc in alkaline media has been investigated by several authors. Most of these investigations have been accompanied on compact metal electrodes or on electrodes made from compacted metal powders; moreover, for the most part such works have been limited to the anodic behaviour of electrodes. For these reasons the present investigations have been more particularly concerned with:

- the various parameters which may be involved in the reduction (charge) of porous cadmium electrodes (sintered nickel impregnated with cadmium hydroxide),
- the effect of such parameters on the performance obtained during oxidation (discharge) at high current densities.

These investigations have enabled us to improve our knowledge of both the operation of negative sintered plates in alkaline nickel-cadmium batteries, and the progress of their characteristics during cycle life, which may be attributed to a passivation process.

3408. Lunn, H. B., Parker, J.

4, 129, (1964)

### Reactions in Sealed Ni-Cd Cells.

The mechanism of oxygen reduction in sealed nickel-cadmium cells has been considered. Experimental evidence showed that the electrolytic reduction on sintered nickel surfaces involved the formation of perhydroxyl. When cadmium was present in the cathode, the chemical reaction between oxygen and cadmium predominated.

The effects on the steady state oxygen pressure of variations in the quantity and composition of the electrolyte, the porosity and state of charge of the active materials, the temperature of the cell and certain features of the assembly have been investigated. Of these the quantity of electrolyte appeared to be the most critical, confirming indications by other workers that the reaction is diffusion controlled. The activation energy of the recombination reaction was estimated.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

The reaction between gaseous hydrogen and the nickel oxide positive active material was also examined. The experiments proved that this reaction took place but at such a low rate that its effect on the gas recombination in sealed cells was insignificant.

3409. Hale, J. M.

4, 147, (1964)

### Kinetics of the $\text{Ni}(\text{OH})_2$ Electrode.

A diffusion controlled mechanism is proposed for operation of the nickel hydroxide electrode. The corresponding boundary value problem in diffusion theory is analysed, and predictions made about the "top of charge", galvanostatic, and potentiostatic electrochemical behaviour of the electrode. The parameters are identified which control the response of the electrode to any perturbation, and means of their experimental determination are described.

3410. Briggs, G. W. D., Fleischmann, M., Thirsk, H. R.

4, 167, (1964)

### The Behaviour of Electrodes of the Second Kind.

The formation and removal of solid phases on metal substrate electrodes ("metallic", semiconducting or insulating phases) is of importance in the operation of most primary and secondary cells. It follows, therefore, that the electrode kinetics of electrodes of the second kind will be an essential part of the overall performance of these cells. The study of this particular aspect of these systems belongs in a general sense to that of the kinetics of electrocrystallization, which has been one of the main subjects investigated in the Electrochemistry Laboratories in the University of Newcastle.

3411. Luciani, C.

4, 419, (1964)

### Field Maintenance of Nickel Cadmium Batteries at Low Temperatures.

This paper describes some effects of low temperature on the maintenance of vented, sintered-plate, nickel-cadmium batteries. Particular attention is given to the methods of charging, battery usefulness and general maintenance. A charging system is described which is compatible with field operation using engine-generator sets. The regulated charging system permits charging of batteries by inexperienced personnel with resulting minimum damage to the batteries. Batteries charged at low temperatures provide an output equal to or slightly more than batteries charged at normal temperatures and discharged at low temperatures. Some field experience with pocket-plate, nickel-cadmium batteries is also included in the paper.

3412. Shair, R. C., Seiger, H. N.

4, 431, (1964)

### Operating Characteristics of Sealed Ni-Cd and Ag-Cd Batteries.

Recent advances in the technology of hermetically sealed nickel-cadmium and silver-cadmium cells have resulted in cells for aerospace use that are capable of a year's operation,



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

about 7000 cycles, in a 100-min cycle of charge-discharge. Reliability assessments in excess of 0.99 have been determined from actual cycle life tests. True hermetic sealing of cell containers has been achieved with welded cases and ceramic-to-metal seals. Complete electrical information has been collected to permit the design of reliable charge control systems. Charge control by voltage has usually been used, but interest is growing in the use of auxiliary electrodes for this function.

3413. Solomon, F., Work, G. W.

4, 463, (1964)

### Present-Day Long Life Silver-Zinc Secondary Batteries.

The silver-zinc battery has been studied to gain a better understanding of its characteristics and to improve its capabilities for secondary battery applications. Factors which limit cell life are discussed as are the effects of cycling regime and certain design parameters. Results of a detailed study of hydrogen evolution are reported. The potentialities of the silver-zinc battery for float applications are shown.

Experimental cells have given as many as 350 deep discharges and 650 shallow discharge cycles. Cell life of up to 2½ years has been demonstrated in cycle service and up to 3 years in float service.

Battery life may be defined in terms of time, cycles or ampere hours discharged until the battery can no longer give a satisfactory output. The silver-zinc battery is not generally considered a long-life battery in time or cycles, but it may equal or exceed other batteries of the same size and weight on the basis of total ampere hours discharged because of its high energy density.

The studies reported reflect several years of development of large, low-rate, silver-zinc batteries. It is intended to show not only the state of the art as it concerns battery life but also the results of some interesting tests not directly related to battery life. Except for the float application, the discussion will be based on cell results, rather than those of multi-cell batteries.

3414. Goodkin, J., Solomon, F.

4, 475, (1964)

### A Zinc-Silver Oxide Cell for Extreme Temperature Application.

This paper describes a zinc-silver oxide battery system for use over the temperature range - 65 to 160 degrees F. The limiting current densities of zinc and argentous oxide electrodes are reported from room temperature down to - 65 degrees F. The electrode utilization efficiencies for both of these electrodes have been measured as a function of the current density over the temperature range of battery operation.

The stability of the electrodes to high temperatures has been established.

A general method of preparation of electrodes for optimum operation over the extreme temperature range is described.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

1966 Symposium Proceedings Published in Power Sources, Edited by D. H. Collins, Pergamon Press (1967).

3415. Dalin, G. A., Stachurski, Z. O. J.

5, 21, (1966)

### Absorption and Diffusion of Zincate Ions in Cellulose Membranes.

Evidence is presented to show that zinc penetration through separators proceeds by growth and not by mechanical puncture. A principal factor in the effectiveness of separators for preventing zinc penetration is therefore the rate of diffusion through the separator. Measurements of the concentration of zincate ion in separators as a function of the concentration in the external solution show a plateau at low zincate concentrations which resembles a Langmuir adsorption isotherm. In this range, the internal concentration is substantially greater than the external concentration. On the assumptions that the membrane zincate is partially adsorbed and partially free and that the log of the zincate activity coefficient at constant ionic strength is a linear function of zincate concentration, an absorption isotherm is derived which gives the adsorbed and internal free zincate as a function of the external zincate concentration. The equation, which involves no arbitrary constants is shown to fit experimental data for regenerated cellulose film. From this equation is calculated the distribution of zincate concentration through the membrane as a function of external concentration on one face, the other face being at zero concentration. The distribution is linear with respect to either face. However, the gradient of the free zincate activity is lower than would correspond to the external zincate concentrations. Zincate growth must occur by deposition of zinc within the membrane, and therefore must be dependent on the permeation rate.

Evidence is presented to show that adsorption takes place only at selected positions on the cellulose chain.

Conception between zincate and surfactants for adsorption sites is demonstrated.

3416. Coleman, J. R., King, T. E.

5, 193, (1966)

### Synthetic Silver Oxide in the Preparation of Battery Electrodes.

Chemically prepared silver oxide ( $\text{AgO}$ ) is used as the depolarizer in electrodes designed for a high-rate primary application. The  $\text{AgO}$ , blended with a few per cent of carbon, is compressed into a plaque on a silver grid, using methyl cellulose as binder. Coulombic efficiencies in the range 75-80 per cent of theoretical are attained on discharge at about  $1.1 \text{ amp/in}^2$ . Variations in preparation designed to increase efficiency are described, as are some characteristics of the resulting plates. The added carbon is thought to act by maintaining electrical contact within the plate during discharge.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3417. Morrell, D. H., Smith, D. W.

5, 207, (1966)

### The Fabrication of Battery Plates Direct From Metal Powders.

An investigation was undertaken to determine the possibility of manufacturing battery plates direct from metal powders as opposed to the present indirect methods of manufacture. The methods of fabrication studied were metal spraying, loose sintering, cold pressing and sintering, and pressing the powders with a filler material added. The technique adopted was to mix a fine metal powder with a water soluble filler and to cold press the mixture. This operation cold welded the individual metal particles together and the filler was then removed to leave a highly porous metal structure.

The work determined (1) the conditions for the production of a mechanically stable plate with a high porosity and (2) the effects of various factors on the electrochemical efficiency of the plate.

It was shown to be possible to produce a zinc plate at least as efficient as a pasted plate and also to be possible to produce lead/acid negative plates.

Further investigations using a slightly different technique produced zinc negative plates having generally very high utilizations.

3418. Harivel, J. P., Morignat, B., Labat, J., Laurent, J. F.

5, 239, (1966)

### Structure and Electrochemical Properties of Nickel Hydroxides.

The chemical or electrochemical oxidation of nickel hydroxide is usually believed to take place in one phase of the Brucite ( $\beta$ ) type in normal conditions. However, some authors have mentioned the possibility of obtaining a nickel hydroxide with a different structure ( $\gamma$  type). The electrochemical characteristics of this last phase and its modes of electrochemical formation were studied in this work.

It was found on the one hand that with sintered electrodes the higher the charging rate, the amount of electricity charged and the electrolyte concentration, the larger the quantity of  $\gamma$ -NiOOH.

On the other hand, with tubular electrodes containing mixed hydroxides of nickel and foreign ions, the  $\beta$  and  $\gamma$  phases always exist together but in variable proportions according to the kind of addition and to the state of charge of the electrode.

3419. Kober, F. P.

5, 257, (1966)

### On Structure of Electrochemically Active Hydrated Nickel Oxide Electrodes.

Thermal analysis of the decomposition of  $\text{Ni}(\text{OH})_2$  is used to determine the hydration state of electrochemically active nickel-oxide electrodes. The effect of thermal decomposition on the electrochemical activity of the electrode provides information concerning the role of hydration in the charge-discharge reaction. The structural changes accompanying the loss of electrochemical activity are determined using infrared spectroscopy and x-ray diffraction techniques. The structural criteria for electrochemical activity of the hydrated nickel-oxide system are discussed.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3420. Weininger, J. L., Breiter, M. W.,

5, 269, (1966)

### The Mechanism of the Cd Negative Electrode.

In this paper, metallographic studies are described first. Photomicrographic, x-ray transmission, and electron beam microprobe techniques show the redistribution of active material in the negative battery plate as a result of repeated cycling. There follows a description of an electrochemical investigation of the anodic oxidation of plane cadmium electrodes and the subsequent reduction of  $\text{Cd}(\text{OH})_2$  and  $\text{CdO}$ . The mechanism of the processes occurring at such an electrode can be discussed in detail. The extent to which it has relevance for the case of the porous plate is also described.

3421. Häusler, E.,

5, 287, (1966)

### Electrochemical Impregnation of Porous Sintered Nickel Grids According to the "Kandler-Process."

In general, the active material is brought into the porous plates by means of chemical precipitation. The processes used therefore differ from each other only with regard to the technical performance and not in the principle on which they are based. But there are also processes based on other principles, e.g., manufacturing of the active material by corrosion of the generally inactive plates. Up to now most of these new processes have not been used economically. The impregnation process developed by L. Kandler, the so-called "Kandler-Process", based on electrochemical reactions, is a new process in which the active material in the pores of the sintered plates does not originate from the grid but from an electrolyte solution. This process has been developed primarily for the manufacture of electrodes for alkaline nickel-cadmium accumulators but it can also be used without any difficulties for the manufacture of highly active catalysts, such as nickel (fuel cells), cobalt, molybdenum, tungsten, etc. incorporated into an inactive grid.

3422. Yamashita, D.

5, 297, (1966)

### The Effect of Lithium and The Formation of Active Material from the Ni Plaque on the Positive Plates of Sintered Type Alkaline Storage Batteries.

Metallic nickel becomes active material as a result of charge-discharge cycles in 25 per cent KOH solution. In the sintered-type alkaline storage battery the capacity of the battery decreases rapidly at the beginning of a charge-discharge test, but before long the capacity increases as a result of the formation of active material from the plaque and therefore the mechanical strength of the plate decreases. Lithium reacts with the active material of the nickel plaque and further reduces the mechanical strength of the plate.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3423. Schneider, F. A.

5, 309, (1966)

### The Anodic Oxidation of Porous Ni Bodies.

Although the possibility of anodically oxidizing porous nickel in  $\text{NaHCO}_3$  solutions has been recognized since 1935, there has been delay in the practical application of the process as a technique for production of plaques for alkaline batteries. Four main factors have impeded development: the high cost of pure nickel grids, the inadequate adhesion of the porous nickel bodies to the grids, the excessive length of time required for electrolysis, and the distortion which occurred in thick plaques during oxidation.

The information given in this paper demonstrates that, as a result of recent research, these difficulties have now been overcome. The conditions essential for successful application of anodic oxidation have been achieved:

- (i) by production of highly symmetrical sintered-nickel plaques in which are incorporated electroformed expanded nickel grids,
- (ii) by accurate correlation of the peak to peak thickness and mesh lattice dimensions of the expanded nickel grid with the thickness of the plaques,
- (iii) by rigorous control of the pH of the electrolyte, and,
- (iv) by use of low-frequency pulsed current, with gradual decrease of current density during electrolysis.

By these means it has proved possible, even with plaques of 3-mm thickness, to obtain, by a one-step process and within 48 hours, a 10-hour capacity of  $5.5 \text{ Ah/dm}^2$ . The cost involved in processing comprises only consumption of gaseous  $\text{CO}_2$ , heat, electricity, and a small amount of a cheap electrolyte. Since the amount of  $\text{CO}_2$  consumed and the heat output depend largely on the design of the equipment used, exact figures cannot be given: maximum consumption of electrolyte would be equal to the pore-volume of the plaques produced. The amount of electricity required to produce a 10-hour capacity of  $5.5 \text{ Ah}$  in a plaque of  $1\text{-dm}^2$  surface area (one side) and 3-mm thickness would be about 0.25 kWh.

3424. Troilius, G., Alfelt, G.

5, 337, (1966)

### The Migration of Iron in Alkaline Nickel-Cadmium Cells with Pocket Electrodes.

During cycling the capacity of the positive active material of an alkaline nickel-cadmium or nickel-iron accumulator decreases. It has long been well known that a contributing reason for this is that iron from different components of the cell is precipitated in the active material of the positive electrode. The iron mainly comes from the positive pockets. In order to avoid this, the iron components of the pockets are nickel-plated. If the negative active material contains iron, this iron will also contribute to the contamination of the nickel mass.

With a radioactive iron isotope it is possible to determine the amount of iron which is transported to the positive active material from different parts of the cell.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3425. Turner, D. R., Howden, W. E., Okinaka, Y. McHenry, E. J. 5, 349, (1966)

### Developments Toward An Improved Sealed Ni-Cd Battery.

In order to insure that the Bell Telephone System will have at its disposal a reliable long-life rechargeable sealed battery for present and future communication applications, a basic development program on sealed Ni-Cd batteries has been carried out. Most of this work was done on cells which were specially designed and made in our own laboratory. Oxygen recombination, the effects of carbonate, and the effects of low and high temperature were studied. Novel and improved methods of preparing electrodes and separator material were developed. Cycle life data on our cells indicate that the sealed Ni-Cd battery system is capable of high reliability and long life.

3426. Peters, F. 5, 371, (1966)

### Sealed Cells of Special Design: Stabilizer Cells, Control Cells, Cells with Control Electrodes: A Survey of Construction and Operating Principles.

Three special designs of sealed alkaline cells are described: Stablizer cells, control cells and cells with control electrodes.

One of the possible designs of the stabilizer cells used for voltage stabilization contains an oxidized cadmium mass in both electrodes. From a certain minimum current the cell voltage of 1.45 to 1.5V at room temperature remains practically constant.

The control cells are similar in construction to these stabilizer cells, but the cadmium mass of the positive electrode is partly reduced before cell assembly. The initial cell voltage of only 50 to 100 mV increases suddenly to approximately 1.5V after complete oxidation of the actual positive electrode. Control cells are used to control the charge and discharge of multicell batteries. When they are connected to these in series, on constant voltage charge, the charging current is reduced abruptly by the rapid voltage increase of the control cell. Since the states of charge of the electrodes have reversed during this process, these control cells can also be used to control the discharge.

The third design relates to sealed cells which are provided with a control electrode connected to one or both of the electrodes by a resistance. The main electrodes have the same balance of the states of charge as the usual sealed alkaline cells i.e. charge and discharge reserves of additional antipolar mass. Oxygen is evolved or reduced at the control electrode at the end of charge or discharge. The voltage drop occurring simultaneously across the resistance, can be used to influence the charge or discharge circuit by means of additional control elements, e.g. relays and the like.

3427. Azulay, M., Kirkman, D. W. T. 5, 399, (1966)

### Some Practical Applications of "Sealed" Ni-Cd Batteries with Charging Arrangements Adopted for Various Operational Regimes.

The paper highlights some of the known limitations of "sealed" nickel cadmium cells both with pocket plates and sintered plates and indicates by practical examples how certain



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

duty cycles have been tackled in the past and what changes, if any, might be suggested for the solution of similar problems in the future.

3428. Gale, R. J.

5, 411, (1966)

### Specialized Development of Sealed Ag-Cd Batteries for Use in Space.

The development of sealed silver-cadmium batteries with characteristics directed towards the specialized requirements of Space use is described. The developments cover the use of new high energy plate systems, improved cell design allowing higher rates of overcharge, and advanced packaging of battery units.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

1968 Symposium Proceedings to be Published in 1969.

3429. Carson, Jr., W. N., Hadley, R. L.

6, 393, (1968)

### Rapid Recharging of Nickel-Cadmium Batteries.

Rapid recharging capability materially increases the utility of secondary batteries by making it possible to reduce the size of the battery required in many applications, and by making it possible to use secondary batteries in applications heretofore blocked by the need for long recharging times. Rapid recharging of vented nickel-cadmium cells is well established; the cell design provides an end of charge signal suitable for reliable control of charging to minimize water losses by electrolysis and overheating caused by excessive rates of overcharging. Rapid recharging of sealed cells requires special control inputs to prevent excessive overcharging of the cell with concomitant unsafe rise in internal gas pressure. Useful inputs are differential voltage input from the cell or battery, auxiliary electrode signals, and coulometer signals. The use of these inputs for charge control and the related circuitry is given; the effect on cell life and behavior is described. Experimentally, tests on very high charging rates appear to show that there is no upper limit on the charging rate that a cell will accept at high efficiency without damage, provided that the cell is not subjected to overcharging at the high rates. Tests were carried out up to the 4000 C rate, which will charge a cell in 1 second. Useful charging rates are determined more by the economic factors involved rather than the technical factors.

3430. Preusse, K. E., Shair, R. C., Betz, F. E.

6, 409, (1968)

### Parametric Charge Studies for Aerospace Nickel-Cadmium Batteries.

One of the most frequently used methods of charge control in a satellite vehicle is a two-step constant current mode. While this mode of recharge is being used today with a high degree of confidence, more data are desired to define the capacity as a function of the charging current, depth of discharge, battery temperature and upper control voltage. This paper presents in parametric form the interrelationship of depth of discharge, upper voltage limit, charging and temperature as a function of capacity returned. The comparison is made for near-earth orbits utilizing conventional aerospace nickel-cadmium cells and third electrode (Adhydrode) cells. The effects of the trickle charge level have also been investigated. Similar information has been produced for the third (Adhydrode) electrode cells. The cells selected on which to perform the experiments were the standard Gulton VO6HS and VO6HSAD 6-A-hr hermetically sealed cells. This size Gulton cell has been used on numerous successful space missions.

From these studies, it can be concluded that:

1. Cells cycled to 20 per cent depth of discharge can be recharged utilizing the conventional two-step charge control scheme.
2. Cells cycled to 40 per cent cannot be recharged using the conventional two-step charge control scheme.



## INTERNATIONAL POWER SOURCES SYMPOSIUM (Cont.)

3. Cells cycled to 40 per cent depth can be recharged at the C or C/2 rate utilizing the Adhydrode charge control concept.
4. Cells cycled to 60 per cent can be recharged at the C rate utilizing the Adhydrode charge control concept.

3431. Lukovtsev, P. D., Malandin, O. G.

6, 423, (1968)

### On the Self Discharge of a Nickel Oxide Electrode.

With a view to establishing the reasons for the discrepancies between the calculated and experimental data on the self-discharge of a nickel oxide electrode (NOE), the behaviour of an oxidized nickel electrode in 11 N KOH in the potential range 0.25–0.55 against the Hg/HgO electrode in the same solution has been investigated by the means of measurements of the galvanostatic  $\phi$ –log  $i$  curves, the potentiostatic  $i$ – $\phi$  curves and of the curves of the potential drop after switching off the current.

It is suggested that the self-discharge of NOE in the potential range below 0.4 V is determined not only by the process of oxygen evolution into the gas phase, but also by the “strengthening” of the oxygen bond in nickel oxides.



INTERNATIONAL SYMPOSIUM ON REACTIVITY OF SOLIDS,  
PROCEEDINGS OF

3500. Feitknecht, W., Wyttenbach, A., Buser, W.

4, 234, (1964)

Tritium Exchange Between Water and The Hydroxides  $\text{Ni(OH)}_2$  and  $\alpha\text{-FeOOH}$ .

It has been shown previously that the first step of the oxidation of the hydroxides of some transition metals may be explained by assuming that  $\text{H}^+$  and electrons diffuse through the crystals to the surface. In order to verify the assumption of a high diffusion coefficient of  $\text{H}^+$  in the hydroxide lattice, the rate of exchange of tritiated hydroxides with  $\text{H}_2\text{O}$  is measured. The average diameter of the crystals was obtained from electron microphotographs, and the surface measured by the BET-method.

In all experiments the ratio between the number of H-atoms in the hydroxide to that in the water was very small ( $\sim 0.01 - 0.003$ ). The exchange in liquid water was performed in small tubes, one tube for every point of the exchange curve. For the exchange in water vapour ( $\sim 0.9 \text{ At}$ ) the hydroxide was shaken in a glass container and samples of the vapour taken out from time to time.

In all experiments a rapid exchange, interpreted as surface exchange, is followed by a slower reaction, due to self-diffusion.

The surface exchange of  $\text{Ni(OH)}_2$ , taken per  $\text{cm}^2$  is much less for a sample with larger crystals (prepared at 200 degrees) than for smaller crystals (prepared at 60 degrees), which is probably due to differences in the perfection of the surface.  $\text{FeOOH}$  shows a 2-3 times smaller surface exchange than  $\text{Ni(OH)}_2$  of comparable surface.

In liquid water the slow exchange of  $\text{Ni(OH)}_2$  is irregular, which is probably due to recrystallisation.

For the exchange of  $\text{Ni(OH)}_2$  in vapour the slow exchange (after correction for the surface exchange) plotted against  $t^{-1/2}$  gives a straight line up to an exchange of  $\sim 0.6$ . This is in agreement with the theory of diffusion in sheets. The temperature dependence of the self-diffusion follows the Arrhenius equation, leading to an activation energy of  $\sim 23 \text{ kcal}$  for  $\text{Ni(OH)}_2$  (between 100 degrees - 160 degrees) and  $\sim 165 \text{ kcal}$  for  $\alpha\text{-FeOOH}$  (between 50 degrees - 174 degrees).



NATURWISSENSCHATTEN, DIE

3600. Lange, E., Ohse, R.

45, 437, (1958)

Determination of Electrode Reactions in the Cadmium Aqueous Solution System  
on the Basis of Intermittent Charging Curves.

As was previously done for silver, lead and iron electrodes, intermittent galvanostatic charging curves were recorded using an oscilloscope for the system cadmium/aqueous solution under  $N_2$ , with agitation,  $25^\circ C$ ,  $pH = 0$  and  $10$  to  $15$ . The oscillogram for  $0.1$  n KOH, anode load (after earlier cathode load), is given as an example. The following reference voltage levels with current flow ( $U_{H,I}$ ) or rest ( $U_{H,R}$ ) were measured in this manner;  $1$  to  $5$  at  $0.1$  n KOH,  $6$  at  $1$  n KOH.



## PHYSICAL CHEMISTRY, JOURNAL OF

3700. Hanson, H. P., Milligan, W. O.

60, 1144, (1956)

### The Ni K Absorption Edges of Oxides of Nickel.

It has been observed that finely-divided nickelous oxide prepared by heat-treatment of nickelous hydroxide exhibits a remarkable enhancement in its room temperature magnetic susceptibility, the susceptibility increasing regularly as the temperature of heat treatment is decreased. More recently, it has been found that these nickel oxide samples exhibit maxima in susceptibility-temperature plots. The temperatures,  $T_c$ , at which the maxima appear, decrease regularly and the amplitudes of the maxima increase regularly, with decreasing crystal size. In the range of crystal size studied (80-2000 Å.), linear plots are obtained for  $T_c$  as a function of  $f$ , the ratio of the average number of next nearest magnetic neighbors per nickel atom to the number of next nearest magnetic neighbors in an infinite crystal, as computed from observed crystal sizes. A complete explanation of this magnetic behavior requires a consideration of the state of oxidation of the nickel ions in the crystals, inasmuch as the finely-divided nickel oxide contains small amounts of "active" oxygen (Bunsen test).

3701. Gayer, K. H., Woontner, L.

61, 369, (1957)

### The Equilibria of Cadmium Hydroxide in Acidic and Basic Media at 25°.

The solubility of cadmium hydroxide has been studied in perchloric acid and in sodium hydroxide solution at 25°. Cadmium hydroxide was found to have fairly strong basic properties but it was also found to exhibit some acidic properties.

3702. Dirkse, T. P., De Vries, D. B.

63, 107, (1959)

### The Effect of Continuously Changing Potential on the Silver Electrode in Alkaline Solutions

When a silver wire is oxidized by continuously increasing its potential in alkaline solutions, four reactions take place. It is suggested that the first is due to the formation of AgOH. The others are due to the formation of  $Ag_2O$ , of AgO and of oxygen. The first and second reactions are indistinguishable in solutions having a high pH. The results show that the formation of  $Ag_2O$  is not due to the action of oxygen on silver, and the formation of AgO does not involve the  $HO_2$ -ion.

3703. Ammar, I. A., Hassanein, M.

64, 558, (1960)

### Hydrogen Overpotential on Cadmium

Hydrogen overpotential has been measured on Cd in 0.01, 0.05, 0.1 N HCl, and in 0.01, 0.05, 0.1 and 0.5 N NaOH. Measurements have been carried out at 20, 30, 40 and 50°



## PHYSICAL CHEMISTRY, JOURNAL OF (Cont.)

The results have been statistically analyzed and the confidence limits have been computed. It has been observed that the Tafel slope lies between 0.16 and 0.18 v., the maximum confidence limits being  $\pm 0.01$  v. The results have been compared with the results of previous authors.

3704. Richardson, J. T.

67, 1377, (1963)

### Magnetic Properties of $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

The valence state of nickel in its higher oxides is in considerable doubt. When chlorine or bromine in alkaline solution is added to a solution of a nickel salt, the result is a black, hydrated oxide with a composition from  $\text{NiO}_2 \cdot x\text{H}_2\text{O}$  to  $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . Cairns and Ott prepared and studied a compound  $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , which decomposed on heating to  $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and then to  $\text{NiO}$ . These authors confirmed the presence of  $\text{Ni}^{3+}$  by X-ray absorption edge measurements, although Hanson and Milligan, performing similar experiments, found no differences between these and  $\text{NiO}$  samples. Cairns and Ott also reported their failure to prepare anhydrous  $\text{Ni}_2\text{O}_3$  by heating the hydrate. Recently, however, Aggarwal and Goswami detected lines in electron diffraction patterns attributed to hexagonal  $\text{Ni}_2\text{O}_3$  on the oxidized surface of nickel films. The existence of nickelic oxide is denied by Vainshtein, who considers  $\text{Ni}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  to be a mixture of hydrated  $\text{NiO}$  and  $\text{NiO}_2$ .

3705. Low, M. J., Kamel, A. M.

69, 450, (1965)

### The Thermal Decomposition of Cadmium Hydroxide.

Differential thermal and thermogravimetric analyses of  $\text{CdO} \cdot 1.65\text{H}_2\text{O}$  showed that four processes were involved in the thermal decomposition. Isothermal weight loss determinations showed that, at 300 degrees and above, the decomposition to  $\text{CdO}_{0.80}$  was continuous. The composition of intermediates is uncertain because of the rapid and continuous reaction. Some oxide was formed as low as 265 degrees. The decomposition was accompanied by marked textural changes of the solid. Surface areas of pure hydroxide as well as samples containing 1 atom %  $\text{Li}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Mg}^{+2}$ , or  $\text{Al}^{+3}$  were measured after heating *in vacuo* for various times at temperatures from 150 to 500 degrees.  $\text{Al}^{+3}$ -addition inhibited and  $\text{Li}^+$ -addition enhanced oxide sintering up to 400 degrees, through the destruction or creation of oxygen vacancies. At 450 and 500 degrees both  $\text{Al}^{+3}$  and  $\text{Li}^+$  additions increased sintering, suggesting that a cation vacancy mechanism became dominant.

3706. Oldham, K. B., Topol, L. E.

71, 3007, (1967)

### Electrochemical Investigation of Porous Media I Theory of Potentiostatic Methods

The measurement of the current following the application of a potential step or potential reversal to a porous material, soaked in a solution containing electroactive species, offers a



## PHYSICAL CHEMISTRY, JOURNAL OF (Cont.)

possible method of studying pure structure. The theory is derived first for a system from which the porous material is absent. Four models of porous matrices are then presented together with modifications which such structures would engender in the electrochemical behavior.



## PHYSICAL REVIEW

3800. Morin, E. J.

93, 1199, (1954)

### Electrical Properties of NiO.

The conductivity, Seebeck effect, and optical transmission of NiO have been analyzed using two alternative models. The first model assumes conduction to occur in the d levels of Ni ions and yields a quantitative fit to the data. Mobility behavior determined with this model is explained in terms of wavy bands. The second model assumes conduction in the filled sp band of oxygen in addition to d-level conduction. It also yields a quantitative fit to the data which, however, is unsatisfactory because the concentrations and mobilities which result for d carriers appear unreasonable. Examples of grain boundary conduction are analyzed.



## POWDER METALLURGY

3900. Tracey, V. A., Perks, R. P.

6, 54, (1963)

### The Structure and Properties of Sintered Carbonyl Nickel Powders.

Four carbonyl-nickel powders with bulk densities between 0.6 and 1.0g/c.c. have been examined and their behaviour on loose sintering in dry hydrogen between 700 and 1000 degrees C assessed. The properties of the porous plates produced were determined from porosity, pore-spectrum, fibre-strength, and electrical-resistivity measurements.

It is shown that the majority of shrinkage occurs in the vertical direction by collapse of the powder bed in the first stage of sintering and that subsequent densification in the second stage is considerably slower. The increase in strength and decrease in electrical resistivity is more rapid in the second stage. The strength and resistivity are related to porosity, indicating a slight preference for a low-bulk-density powder when considering porosities in the range between 80 and 90%.

Limited consideration is given to the effects of restraint and of atmospheres other than dry hydrogen, but although these modify the sintering behaviour the relationships with porosity obtained with dry hydrogen appear to hold.

3901. Tracey, V. A.

8, 241, (1965)

### Production of Porous Nickel for Alkaline-Battery and Fuel-Cell Electrodes: Practical and Economic Considerations.

A review is given of the requirements that must be met by porous nickel for alkaline-battery and fuel-cell electrodes. Methods by which the desired properties can be achieved are considered. Specific reference is made to four production techniques which may be employed singly or in combination. Practical and economic considerations involved in the use of the respective processes are discussed.

3902. Tracey, V. A.

9, 54, (1966)

### The Properties and Some Applications of Carbonyl-Nickel Powders.

Nickel carbonyl, formed by the reaction of carbon monoxide with a nickel concentrate, can be decomposed in a heated space to produce pure nickel in powder form. By varying the decomposition conditions it is possible to achieve a wide range of powders, differing in particle shape and size distribution.

The properties of carbonyl-nickel powders now commercially available or in an advanced stage of development are discussed, and it is shown how such powders can be used for some applications in which specific properties are required.



## POWDER METALLURGY (Cont.)

3903. Bagshaw, N. E., Barnes, M. P., Evans, J. A.

10, 13, (1967)

### The Properties of Porous Nickel Produced by Pressing and Sintering.

The effects of compacting pressure and of sintering temperature and time on the properties of porous sintered nickel compacts have been studied, using three carbonyl and two reduced nickel powders. For all five powders, the density of the green compacts and the porosity of the sintered compacts were linearly related to the log compacting pressure. Similar relationships with pressure were observed for strength and electrical conductivity.

Photomicrographs of sections through the sintered compacts made from the reduced nickel powders show that there are pores in two different size ranges, originating from the porosity between the original powder particles and the pores within the particles. It is concluded that sintered compacts from all five powders containing 40-50% porosity have adequate strength and conductivity for use in fuel-cell electrodes.



POWER SOURCES CONFERENCE\*, PROCEEDINGS OF

4000. Dehmelt, K., Von Döhren, H. 13, 85, (1959)

Cathodic Oxygen Reduction Under Conditions, Effective in Hermetically Sealed Nickel-Cadmium Cells.

With cathodes consisting of porous nickel - or cadmium-plaques the dependence of the rate of oxygen reduction on the oxygen pressure and on the applied potential has been determined. In all experiments an immobilized electrolyte was used and the temperature kept constant.

4001. King, T. E., Casey, E. J., Henderson, H.S. 16, 108, (1962)

Canadian Research on Secondary Batteries.

This paper is an attempt to interpret the results of recent research in terms of battery operation, maintenance or design. Only the bare conclusion or summary of each study is given, and reference is made to the original paper. The investigations reported include not only those of this Laboratory, but also those done at Canadian Universities with the support and encouragement of the Defence Research Board's grant-in-aid-to-research program. No information published before 1960 is included in this review although references to earlier work are given. Much of the current information is still in the process of publication. Only the three standard secondary systems are reviewed.

4002. Cupp, E. B. 17, 105, (1963)

Sealed Nickel-Cadmium Batteries.

During the past three years, The Eagle-Picher Company has conducted research investigations in an effort to develop a more reliable sealed nickel-cadmium battery. The first two years of work were supported by Lockheed Missiles and Space Company and the Air Force SSD, and the efforts during the past year have been supported by USAELRDL.

4003. Resnic, B. 17, 107, (1963)

Optimum Charge Procedures for Sealed Nickel-Cadmium Batteries.

Under this program we plan to study the constant potential, constant current, and pulse charging techniques. At present, modifications of the constant current and constant potential methods are not being considered. The relative importance of certain charging conditions and how these effect overall cell performance is to be determined. Included in the program are the effects of charging times of 1, to 16 hours, the effects of ambient temperatures of  $-40^{\circ}\text{F}$  to  $+125^{\circ}\text{F}$ , and the influence of initial battery states of charge of 0 to 66%. The effects of from 10 to 70% overcharge in the constant current method, effects of voltage level in the constant

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## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

potential method, and variations in pulsing in the pulse charging method are also included. Two cell types, the 3.5 A.H. and 10 A. H. cells, and two discharge rates, the 15 minute and the 5 hour rates are other study parameters.

4004. Lurie, M., Seiger, H. N., Shair, R. C.

17, 110, (1963)

### State of Charge Methods for Nickel-Cadmium Batteries.

Many efforts to measure state of charge of nickel-cadmium batteries have been reported in the literature. Recent work has included studies of (i) dyes, (ii) charge and discharge characteristics and (iii) impedance at audio frequencies by Fleischer, and (iv) a very extensive study of charge-discharge tests by Kordes and Kornfeil. Fleischer concluded that none of the techniques he studied were acceptable state-of-charge indicators. Kordes and Kornfeil devised a means of measuring the polarization resulting from charge or discharge without the effect of the internal ohmic resistance of the cell. Kordes incorporated this technique into a battery tester based on charge-discharge characteristics. Prototypes of this tester were built by the Vitro Corporation and were put through extensive tests by Gulton Industries under contract to the Signal Corps (Contract No. DA 36-039 SC-85066). The conclusion reached at the end of those tests was that the device is not an acceptable battery tester.

We have studied the electrical properties of nickel-cadmium cells to determine which, if any, depend on state of charge. In particular, we investigated

1. Phase shift of cell voltage compared to current.
2. Ohmic resistance during a short, high current pulse.
3. Double layer capacitance.
4. Height of transient following a sudden change in current.
5. Magnitude of impedance at audio frequencies.

Both ohmic resistance and phase shift were found to vary in a useful way with state-of-charge and these are discussed.

4005. Frink, Jr., A. M.

17, 114, (1963)

### Sealed Cadmium-Silver Oxide Batteries.

Last year at the Power Sources Conference, I discussed the sealed cadmium-silver oxide system using information supplied by the various manufacturers and users of sealed cadmium-silver oxide batteries. At that time I included a review of the merits of the system, construction details, problems encountered and cycle life data. Today I will present another survey showing the accomplishments that have been made in sealed cadmium-silver oxide batteries from last year to the present. It will cover the following:

1. A brief review of the system
2. Recent developments
3. Cycle life data



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4006. Keralla, J. A., Lander, J. J.

17, 116, (1963)

### Sealed Zinc-Silver Oxide Batteries.

The battery development and test phase of a program directed at obtaining an hermetically sealed zinc-silver oxide secondary battery for aerospace applications has been completed. Two previous papers in this series have been given at this Conference: the first dealt with cell component studies, the second with sealed cell studies. This paper concerns cycle-life testing of hermetically sealed batteries.

4007. Dirkse, T. P.

17, 120, (1963)

### Separators for Alkaline Batteries.

One of the drawbacks to the more widespread use of the silver-zinc-alkali battery is the fact that the silver oxides are soluble in the KOH electrolyte. Because of this, silver can be transferred to the zinc plates of the battery and eventually cause internal shorting. This transport of silver can be, and is, lessened by the use of separator materials. However, after cells have been cycled for some time there are likely to be extensive silver deposits on or in the separators. If these deposits build up they can lead to internal shorting. In many instances the separators, in effect, delay the building up of internal shorts due to silver to such an extent that cell failure is then due to other causes.

4008. Ingling, W. G., Clark, W. W.

17, 122, (1963)

### Evaluation of Secondary Batteries.

In 1960 a large-scale program of space battery evaluation was initiated by the Air Force through the present Aeronautical Systems Division at Wright-Patterson Air Force Base. The primary objectives of this program were two-fold. First, a broad base of data on the performance characteristics of sealed, secondary batteries was desired to determine the probable useful life of these units when subjected to the various load conditions and many temperature environments that they may encounter in aerospace applications. Secondly, a chemical and physical analysis of cycled cells was desired in order to determine the nature and extent of failure mechanisms so that research efforts could be directed toward increasing the reliability, cycle life, and energy density.

4009. Settembre, E. J.

18, 41, (1964)

### Standard Line of Secondary Batteries.

This presentation will review activity during the last year in the design and development of a standard line of alkaline secondary batteries. The concept of standardization is well imbedded in our daily thinking and plays an important and significant role in the industrial and



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

military makeup of our country. Thus, it has also been a part of former programs in primary and secondary batteries. However, in secondary batteries it had not gone beyond standardization of single cell batteries and this to a limited extent only. The present program is far more extensive and ambitious and is intended to go well beyond cell standardization.

4010. Cupp, E. B.

18, 44, (1964)

### Sealed Nickel-Cadmium Batteries.

Investigations carried out previously, and covered in a paper given at the Seventeenth Power Sources Conference, indicated improvement could be effected in some of the foregoing areas by the use of electrolyte additives and sponge cadmium plates. In view of these possibilities, a designed experiment was constructed. The designed experiment consisted of four sets of twenty-seven cells which were built to the dimensions of a standard ten ampere-hour design.

4011. Kroger, H. H.

18, 46, (1964)

### Characterization of Sealed Nickel-Cadmium Cells.

The objective of our experiments was to study the influence of the amount of the electrolyte, of the concentration of the electrolyte and of the separator materials respectively, on the pressures, potentials and capacities of sealed nickel-cadmium cells over an extended period of time.

4012. Shair, R. C., Liska, J., Rampel, G.

18, 50, (1964)

### Silver-Cadmium Batteries.

During the past year, further separator development has resulted in a modified cellulosic separator which, in combination with non-woven electrolyte retaining separators, has resulted in a highly effective three-ply separator. The new separator has reduced electrical resistance, and the silver-cadmium cells utilizing it have improved voltage characteristics.

Overcharge capability, which has always been lower for silver-cadmium sealed cells than for nickel-cadmium cells, has seen a significant enhancement due to the incorporation of Adhydrodes, auxiliary recombination and control electrodes, into the sealed cells.

Additional electrical data and cycle life information have been collected on both sealed and vented silver-cadmium cells.



POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4013. Dalin, G. A., Sulkes, M., Stachurski, Z.

18, 54, (1964)

Sealed Silver-Zinc Batteries.

The principal objective of this program is the development of silver-zinc batteries which can function sealed over a wide range of conditions. As is generally the case with electrochemical systems, gases may be produced in normal operation. Difficulty arises only because the silver-zinc cell requires semi-permeable separator and a substantial amount of free electrolyte which is needed for satisfactory charge and discharge. The free electrolyte and the membranes hinder access of gas to the electrodes and thus decrease the rate at which gas recombination takes place. The problem of the pressure rise which may ensue is only one phase of the program but the information which has been developed appears to us to warrant presentation at this time. In this study we have aimed at determining fundamental mechanisms, because an approach through specific devices can be inconclusive.

4014. Carson, Jr., W. N.

18, 59, (1964)

Charge Control for Secondary Batteries. Part I. Auxiliary Electrode  
for Charge Control.

This paper presents some of the work my colleagues and I have done in the past two years on auxiliary charge control systems for nickel-cadmium cells and batteries. The use of this type of charge control allows very rapid charging of sealed cells; we have for example used rates as high as 10C successfully. However, the use of rates greater than 2 to 3C is generally uneconomic, since the power supply must be designed to deliver the required d. c. currents. At high charging rates, the cost of these high-current supplies is not trivial, and is only partly off-set by the elimination of voltage or current limit controls. The use of 1 to 2C rates is satisfactory in most commercial applications; the use of higher rates for military or space applications is dependent upon the application.

4015. Seiger, H. N., Shair, R. C., Ritterman, P. F.

18, 61, (1964)

Charge Control For Secondary Batteries. Part 2 - The Adhydrode in Charge Control.

There are three requirements for an auxiliary electrode in order for it to function as an Adhydrode. It must (1) be at a potential in the neighborhood of -0.8 volts; (2) be covered with a film of electrolyte and (3) be readily accessible to oxygen. To meet the first requirement the auxiliary electrode is connected to the cadmium electrode through a relatively low resistance path. The second requirement is met by using a somewhat greater amount of electrolyte than is normally used in this laboratory for sealed cells. The third requirement is met by the physical location of the Adhydrode within the cell.



POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4016. Cocca, F. J.

18, 65, (1964)

Stabistors - Their Application in Battery Operation.

The Adhydrode is an electrode which contains hydrogen atoms, interstitially as well as on its surface. When oxygen reaches the surface of such an electrode it is reduced by reaction with hydrogen atoms. The Adhydrode mechanism occurs on several catalytic materials at a potential of -0.8 volts (NHE). Silver is an example of an electrocatalyst that may exhibit the perhydroxyl mechanism or the Adhydrode mechanism for oxygen reduction. Which mechanism prevails depends upon the potential. The perhydroxyl mechanism takes place at a silver electrode (in 8N KOH at room temperature) in the neighborhood of +0.2 volts.

4017. Ho, J. W.

18, 68, (1964)

Nuclear Radiation Resistant Batteries.

The advent of nuclear powered space flights within this decade imposes new problems upon the spacecraft equipment designers. In addition to fulfilling the usual requirements encountered in space and during launch periods, equipment on board these nuclear powered flights must also resist the degrading effects of nuclear radiations emitted from the nuclear sources. Unless these equipments are designed to withstand these nuclear radiation effects, possible failures may occur. In batteries, nuclear radiation effects usually manifest themselves in material degradation and eventual failures. In extreme cases, materials failure in key components such as separators, seals, and cell cases can lead to potential hazards. It is therefore prudent to scrutinize closely the materials used in the design of these space batteries which are intended for service on board nuclear powered spacecrafts.

4018. Stroup, E. R., Apelt, A. O.

19, 56, (1965)

Secondary Battery Evaluation Program.

The primary objective of this program is to gather characteristic information and performance data regarding electrochemical secondary cells that can be used by Engineers and Scientists in designing and building power supplies for space applications. Space batteries with the most recent developments incorporated therein are placed in the program in sufficient numbers to provide information in sufficient depth to adequately support basic power supply design decisions.



POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4019. Grieger, P. F.

19, 58, (1965)

Evaluation of Auxiliary Electrode Materials.

The idea of using auxiliary electrodes to consume the gases in hermetically sealed cells dates back to the 1930s but S. S. Jaffe, about ten years ago, while working in the Thomas A. Edison Research Laboratory, was the first to propose making the current (that flows through the external connection between the main cadmium and an auxiliary  $O_2$  reduction electrode) do useful work by powering a relay arranged to terminate charging of the cell.

4020. Catotti, A. J., Read, M.D.

19, 63, (1965)

Charge Control of Nickel-Cadmium Batteries. Auxiliary Electrodes  
for Overcharge and Overdischarge Control.

Hermetically sealed nickel-cadmium batteries have proven to be the most reliable energy storage system for aerospace applications. Conventional sealed nickel-cadmium cells can be safely overcharged only at moderate rates ( $C/10$  to  $C/7$ ). Consequently when constant current charging is employed the depth of discharge is severely limited on short cycles. In order to overcome this limitation, the use of auxiliary gas electrodes has been suggested as a means of charge control. The development of practical units having auxiliary gas electrodes as control electrodes to detect the onset of overcharge has been described previously. This is generally accomplished by: (1) building a cell which is positive limiting on charge; (2) incorporating a gas electrode connected to the negative terminal by an external impedance; and (3), regulating the charge when oxygen is generated on overcharge by monitoring the signal voltage or current between the control electrode and the negative electrode. Such units are capable of being charged at very high rates and thus under a given set of conditions can be used at a greater depth of discharge.

4021. Amsterdam, R. E.

19, 66, (1965)

Charge Control of Nickel-Cadmium Batteries.

The Amp-Gate Diode is a specially designed stabistor diode developed by P. R. Mallory for overcharge protection of secondary cells. (Its forward characteristic is employed to equalize the voltage across series operated secondary cells during charging.) The diode acts as a voltage-sensitive gate to shunt the charging current around each cell as each cell reaches full charge. This type of charge control device has the advantage of bringing all the cells in a battery, in spite of variations in capacity or state of charge, to their fully charged state at the end of each charge cycle without subjecting them to the damaging conditions of overcharging and consequent gassing.



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4022. Dalin, G. A., Sulkes, M.

19, 69, (1965)

### Sealed Zinc-Silver Oxide Batteries, Part I.

The work on this program was directed toward development of reliable high performance sealed silver-zinc cells. Specific requirements were that the units should exhibit good voltage and capacity over a wide temperature range. Also, good cycle life should be obtainable on a cycling regime consisting of a 2½ hour discharge of 62½% of nominal capacity with recharge in 3½ hours. Moreover, the energy densities obtained must be characteristic of the silver-zinc system, and above all, the system must be free of the problems of excessive pressure rise.

4023. Wylie, G. M.

19, 73, (1965)

### Sealed Zinc-Silver Oxide Batteries, Part II.

Over the past four years the Missile Battery Division of The Electric Storage Battery Company has been actively developing sealed silver oxide-zinc batteries for use in space systems.

4024. Lander, J. J., Keralla, J. A., Scardaville, P. A.

19, 77, (1965)

### Sealed Zinc-Silver Oxide Batteries, Part III.

The problems associated with the use of commercially available materials of the cellulose type when used as separators in the secondary silver-zinc battery are well-known. They degrade in the strongly alkaline electrolyte by alkaline hydrolysis; they are oxidized by oxygen or other oxidizing agents which may be formed at the zinc plate on charge; they "pick up" metallic silver either by reaction with soluble silver oxides or trapping of colloidal silver, especially in the layer next to the positive plate; and, they permit the growth through them of dendritic zinc from the negative plate. All such behavior promotes failure by short-circuiting and, consequently, the commercial cellulose are not suitable for use in long-lived secondary batteries except in multiple layers. The total thickness of these multiple layers becomes an appreciable factor in the weight and volume of the cell when used in sufficient thickness to discourage failure by short-circuiting. For example, the necessary thickness (swelled) of fiber-strengthened sausage casing may well be double or more than double the thickness of the positive plate itself, in long-lived designs.

4025. Nagy, G. D., Moroz, W. J., and Casey, E. J.

19, 80, (1965)

### Studies on the Stability of Oxides of Silver.

Evidence for the existence of certain oxides of silver is incomplete, in some cases even misleading, but is usually provocative. Good reviews of the energetics, electrochemistry and



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

kinetics are available. The monovalent oxide is the best understood, both physically and chemically. Normal  $\text{Ag}_2\text{O}$  is the most stable of the silver oxides, is used as a catalyst for many reactions, and is incorporated directly in  $\text{Zn}/\text{Ag}_2\text{O}$  and  $\text{Cd}/\text{Ag}_2\text{O}$  cells by several manufacturers. A high pressure form with  $\text{CdI}_2$  structure, a metallic lustre, and much higher electrical conductivity, was recently reported.

4026. Dalin, G. A., Sulkes, M.

20, 120, (1966)

### Design of Sealed Ag-Zn Cells.

The work on this program was directed toward the development of reliable, high performance, high energy density, sealed silver-zinc cells. Specific requirements were that the units should exhibit good voltage and capacity over a wide temperature range, and that good cycle life should be obtainable on a cycling regime consisting of a  $2\frac{1}{2}$  hour discharge of 62½% of nominal capacity with recharge in  $3\frac{1}{2}$  hours. The overriding problem was the development of a design which could cope with the gases produced during cycling and stand. Pressure buildup in a sealed Ag-Zn cell can be caused by hydrogen generation, largely on stand or by gas generation during overcharge or discharge. Cell design and aging processes are such that oxygen is generated both at the end of charge and discharge.

4027. Oxley, J. E., Fleischmann, C. W., Oswin, H. G.

20, 123, (1966)

### Improved Zinc Electrodes for Secondary Batteries.

The deterioration of silver-zinc secondary batteries and the relatively short cycle-life is largely attributable to changes occurring in the zinc electrode structure as a result of discharging and re-charging. These changes appear as two major effects—the formation of dendritic zinc and the build-up of non-adherent zinc deposits. The latter effect, non-adherency, leads to a loss of negative plate capacity and perhaps in some cells to the formation of free zinc particles in the electrolyte. The effects of dendritic formation are less easily observed, but this phenomenon is believed to be responsible for internal cell shorts which cause complete failure and loss of capacity in all the plates of a cell. These shorts are probably dendritic, dense zinc “bridges” which protrude from the zinc electrode, penetrate the separator and contact the positive plate.

4028. Consiglio, J. A.

20, 126, (1966)

### Electrodeposited Inorganic Separator for Ag-Cd Batteries.

In recent years there has been considerable effort directed toward improving separator materials for application in secondary silver-oxide-cadmium and silver oxide-zinc cell. Most of this work has been concerned with cellulosic and synthetic organic polymer materials. More recently, separators based on the use of inorganic materials have also been reported. The approach discussed in this paper is the use of inorganic films of calcium or magnesium hydroxide



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

for the separator functions. The novel feature of the approach is the electrochemical application of the materials in film form directly on to electrode substrate. The objective of the current program is to evaluate the use of these films as separators in silver oxide-cadmium cells. The potential gains to be made with the successful development of these separators are increased chemical stability at elevated temperatures and a reduction in silver migration. Since the program is still in progress, this paper is a status report of the work accomplished to date.

4029. Waite, J. H.

20, 130, (1966)

### Performance Prediction for Ni-Cd Batteries.

This paper is concerned with an analysis of the Crane test data and assumes that the reader is acquainted with the Crane Life-Cycle Test Program. The specific objectives of this analysis are:

1. To identify digital patterns in the test data.
2. To associate these patterns uniquely with cells which failed or succeeded.
3. To determine if such associated patterns could be used to predict cell failure early enough to develop a nondestructive cell selection procedure.
4. To associate the patterns indicating failure to failure modes.
5. To identify digital patterns which indicate faulty monitoring equipment.

4030. Turner, D. R., Willis, T. H.

20, 133, (1966)

### High Temperature Effects on Sealed Ni-Cd Batteries.

There are several present and future applications in the Bell System for sealed rechargeable batteries which will operate reliably with good life over a wide range of ambient temperatures from  $-40$  to  $60^{\circ}\text{C}$  ( $140^{\circ}\text{F}$ ). At the present time, the sealed Ni-Cd battery best meets the requirements. Gottlieb and Willis<sup>1</sup> studied the low temperature effects in sealed Ni-Cd cells. This paper will describe the results of experiments on sealed Ni-Cd cells at elevated temperatures.

4031. Jost, E. M., Popat, P. V.

20, 136, (1966)

### Improved Sealed Ni-Cd Cells.

When Metals & Controls Inc., a division of Texas Instruments Incorporated, initiated a research project on batteries with emphasis on hermetically sealed Ni-Cd cells, it became quickly apparent that battery experimentation presented several very complex problems. Sealed Ni-Cd cell systems are not amenable to the successful application of analytical and inductive methods. Empirical approaches are more promising.

For the same pore filling by electrolyte the combinations containing less Cd show lower equilibrium voltages, viz, 1.685V and 1.835V for combinations (00) and (01), respectively.



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

4032. Bradshaw, B. C.

20, 140, (1966)

### Self Discharge on $\text{Ni}(\text{OH})_2$ Electrodes.

It seemed to us that the chief hindrance to the development of any reliable method for the determination of the ratio of the oxidized to the reduced material on the positive electrode of cells in general (except the lead acid cell), and the nickel-cadmium cell in particular was the lack of an adequate theory, therefore we began a study of the nickel-cadmium cell. As a result of this study we have developed a theory which explains all of the data for the nickel-cadmium cell that we can find, and in addition gives four methods for determining this ratio on the nickel oxide electrode. We believe that both our theory and methods are applicable to a wide range of cells.

The four methods that we have developed, and tested, for the nickel-cadmium cell are:

1. Measure the volumes of oxygen that are spontaneously evolved as a function of the time and the temperature.
2. Measure the electromotive force of the cell on open circuit as a function of the time and the temperature.
3. Measure the electromotive force of the cell on open circuit as a function of the volumes of oxygen that are spontaneously evolved, and the temperature.
4. Measure the electromotive force and the number of electrons that are added to, or taken from, the nickel oxide electrode and the temperature.

4033. Kroger, H. H., Consiglio, J. A.

20, 145, (1966)

### Gassing Behavior of $\text{Ni}(\text{OH})_2$ Electrodes.

Investigations were reported previously dealing with the influence of charge rates and operating temperatures on the gassing behaviour of flooded nickel hydroxide impregnated nickel sintered electrodes.

Stationary conditions with respect to the onset of measurable oxygen gassing were generally observed after a few repetitive cycles at a given set of operating conditions.

Since that time considerable progress in the application of oxygen detecting and measuring devices on the problem at hand has been made. We are going to discuss two novel instrumentations and a previously used one, and we will present recently obtained data.

4034. Goldberg, P.

21, 70, (1967)

### Nickel-Zinc Cells, Part I.

Of the four possible electrochemical couples that can be formed from silver or nickel positive and zinc or cadmium negative electrodes, only one has remained relatively undeveloped, that is, nickel-zinc. The relative neglect of this couple is surprising in view of the properties of



## POWER SOURCES CONFERENCE, PROCEEDINGS OF (Cont.)

cells that can be projected from the known behavior of the nickel and zinc electrodes. It is reasonable to expect from nickel-zinc cells:

- good energy density (15-30 Wh/lb.)
- higher discharge voltage than the other alkaline couples
- a single voltage plateau during discharge
- favorable electrode kinetics, i.e., good performance at high rate and low temperature.
- life of 100 or more cycles
- moderate cost

4035. Broglio, E. P.

21, 73, (1967)

### Nickel-Zinc Cells, Part II.

Our first attempts at developing a practical battery met serious resistance from a phenomenon which was blanketed under the term "zinc poisoning". The cells merely stopped working as a battery after only a few cycles and acquired the charge characteristics of a variable resistor. Charging currents developed what appeared to be a charge response, however, little energy was stored in the cells. This phenomenon was attributed to zinc complexing of the positive plate. Essentially, our work on the battery was continued sporadically until a particular combination of films offered a hope for limited success. At about this same time, there appeared a resurgence of interest in this battery system as evidenced by the papers being presented here and the foreign literature on the subject. As the data is presented, we think it indicates that the nickel-zinc battery can have some outstanding features and an area of application in the expanding battery field.

4036. Popat, P. V., Rubin, E. J., Flanders, R. B.

21, 76, (1967)

### Nickel-Zinc Cells, Part III.

The nickel-zinc storage battery is old in general concept. However, there is little published information on this system. A technical and economic analysis of the various secondary battery systems revealed that the potential of the nickel-zinc system has not been fully realized and exploited in the United States although rechargeable, vented type nickel-zinc batteries have been used in the Soviet Union for the past many years. Because of the potentially high energy density and relatively low cost of the nickel-zinc battery compared to other alkaline storage batteries, we at Texas Instruments have undertaken a systematic study of this system to gain a better understanding of its performance characteristics, to determine the major problem areas and to improve its capability for sealed, secondary battery applications. This paper gives our preliminary results on the performance characteristics of the nickel-zinc batteries with emphasis on the technical problems associated with this system.



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4037. Goodkin, J.

22, 79, (1968)

Stable Zinc Electrodes.

"Shape change" has been the single reason for the electrode's inability to maintain capacity over extended cycling. This phenomenon has been known by many names which are used to describe the change in the geometric area of the zinc electrode with use. Early theories attributed this phenomenon to a gravitational effect, since toward the end of life, all zinc was found at the bottom of the cell. McBreen was able to show, however, that potential differences across the plate, rather than gravity, were the culprit. In fact, studies conducted during the course of this program have shown that once the oxide is physically immobilized, zinc migrates toward the center of the plate, and not the bottom.

4038. Himy, A.

22, 82, (1968)

Performance with Stable Separators.

It appears, therefore, that an inorganic material insensitive to both alkali and oxidants may have a definite value in improving silver-zinc cell performance if it could be used in fabricating a separator.

More specifically, the paper will deal with their application to silver-zinc batteries and will measure the value of the separator by its performance and characteristics in actual tests.

4039. Sulkes, M. J.

22, 85, (1968)

Improved Army Silver Zinc Batteries.

Uncharged long life silver-zinc cells have been developed that can be ready for use within 24 hours after filling. Improvements have been made to the BB-622/u battery so that the cost per hour of service is less than 1/3 that of the original design. Activation time for this battery has been reduced from approximately 2 weeks to 72 hours, with further reductions possible. In view of the foregoing results, the dry uncharged system would appear to be optimum for most Army applications requiring silver zinc batteries.



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4100. Lukovtsev, P. D., and Slaidin, G. Ya.

36, 1227, (1962)

Oxygen Overpotential and Potential Decay Curves at the Nickel Oxide Electrode.

The use of curves showing the change in potential  $E$  with time  $t$  after the polarising current has been switched off, in order to obtain data on the kinetics of an electrochemical process, has been discussed in several papers. The general case was examined by Grahame, who derived an equation for the potential decay curve when there are several limiting stages in the process. However, his equation proved to be too complicated for practical application.

4101. Tsinman, A. I.

37, 714, (1963)

Effect of Alkali Concentration on Oxygen Overvoltage and Anodic Evolution of Oxygen on Nickel.

Many papers have been written on oxygen overvoltage in alkaline solutions. We have made a study of the overvoltage  $\eta$  of Ni in NaOH and KOH solutions, with special emphasis on the effect of alkali concentration on the overvoltage and on the effect of preliminary oxidation of the electrode on the slope of the polarisation curve.

A partial discussion of the results obtained with an oxidised Ni anode has already been published.

4102. L'vova, L. A., Fortunatov, A. V.

37, 921, (1963)

Anodic Oxidation of Cadmium in Concentrated Alkali's. I.

In spite of the considerable amount of work done on the anodic oxidation of metals in alkalis, the mechanism of this process is still not entirely clear. The most detailed study has been made of the anodic behaviour of iron in alkalis, for which a sound kinetic scheme has been suggested. Very similar conclusions were reached for the anodic oxidation of copper in concentrated alkalis. In our opinion, however, greater attention should be paid to a kinetic scheme in which singly charged ions of atomic oxygen are formed as an intermediate stage. In order to test the general validity of the proposed kinetic scheme, a study has been made of the anodic oxidation of cadmium in concentrated alkalis. The investigation was made by determining potentiostatic polarisation curves, and also curves of the differential capacitance and the resistance of the electrode.

4103. Fortunatov, A. V., L'vova, L. A.

37, 924, (1963)

Anodic Oxidation of Cadmium in Concentrated Solutions of Alkali, II.

The present paper deals with the active state of the cadmium electrode during anodic oxidation in concentrated solutions of alkali. The investigation was carried out by an a.c.



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(Cont.)

method and by determining galvanostatic polarization curves. The circuit of the apparatus, the cell, and the experimental technique have already been described in detail. The galvanostatic polarisation curves were obtained at increasing current densities. The time interval between the measurements of the current density and the potential was 1 min. Increase of the interval to 10 min did not alter the shape of the polarisation curves but the passivation took place at lower current densities. The potential was measured by the usual compensation method with an accuracy of up to 0.5 mV.

4104. L'vova, L. A.

37, 1144, (1963)

Anodic Oxygen Evolution on Cadmium in Concentrated Alkaline Solutions.

Recent advances in electrode kinetics have found extensive application in theoretical studies of the kinetics of anodic oxygen evolution, and have created a need for new diagnostic experiments to test the mechanisms suggested for this process. The study of anodic oxygen evolution on cadmium in concentrated alkaline solutions is highly relevant in this respect. Such investigations have also proved fruitful in the past in explaining various anodic oxidation processes and metal passivation phenomena, and it seems highly probable that they will also lead to a better understanding of the mechanism of anodic oxidation of cadmium, particularly since extensive oxidation of cadmium has been reported to take place immediately prior to oxygen evolution.

4105. L'vova, L. A., and Fortunatov, A. V.

37, 1147, (1963)

Anodic Oxygen Evolution on Cadmium in Concentrated Alkali Solutions.

Some further results on the evolution of oxygen on cadmium in alkaline solutions, obtained by plotting galvanostatic polarization curves and measuring the oxygen evolved, are reported.

4106. Knaster, M. B., and Apel'baum, L. A.

38, 120, (1964)

Solubility of Hydrogen and Oxygen in Concentrated Potassium Hydroxide Solution.

Several papers have been published on the solubility of hydrogen and oxygen in pure water at atmospheric pressure and above, but too few data are available on the solubility of these gases in caustic potash solutions. In connection with research on gas-diffusion electrodes for fuel cells containing an alkaline electrolyte, it became necessary to determine the solubility of these gases in concentrated solutions of potassium hydroxide at various temperatures.



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(Cont.)

4107. Lukovtsev, P. D., and Slaidin, G. Ya. 38, 299, (1964)

Rate of Diffusion of Protons in Nickel Oxides and Oxygen Overpotential  
at a Nickel Oxide Electrode.

Previous papers have given results for the variation of the rate of diffusion of protons in nickel oxides with partial and solution composition in LiOH, NaOH, and KOH. The present paper reports a further study by the previous technique of the diffusion of protons in nickel oxides, in particular of the effect of impurities present in solution on the rate of diffusion of protons and on the overpotential accompanying the evolution of oxygen.

4108. Uflyand, N. Yu., Pozin, Yu. M., and Rozentsueig, S. A. 39, 175, (1965)

Effect of Electrolyte Concentration of Behaviour of Nickel Oxide Electrode.  
I. Physicochemical Properties of the Nickel Oxide-Oxygen System.

Several thorough investigations have been made of the properties of the nickel oxide electrode in an alkaline accumulator. However, this system is so complicated that no generally accepted view yet exists concerning the mechanism of the processes occurring at the nickel oxide electrode. It appeared necessary to study the physicochemical properties of the nickel oxide-oxygen system as a function of the alkali concentration, and this was the main purpose of the present work.



## UNIVERSITY DISSERTATIONS

4200. Salkind, A. J.

Polytechnic Institute of Brooklyn, (1958)

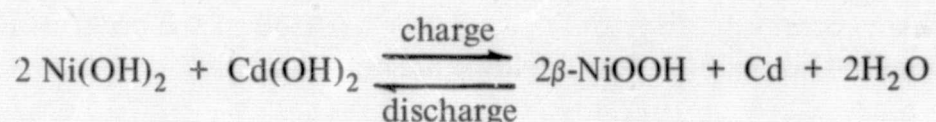
### Investigation of the Nickel Cadmium Cell.

The purpose of this investigation was to determine the reactions and the kinetics of the Nickel-Cadmium cell and to develop a separator material which would be unaffected by the presence of copper impurities in the cell electrodes.

The solid reaction products of the Nickel-Cadmium electrodes were studied by X-ray techniques. Special equipment and methods were developed which permitted X-ray films and diffractometer patterns to be obtained from the electrodes, wet with alkali, while in service and in any state of charge or discharge. Open circuit voltage decay measurements were obtained at temperatures between 0°F and 125°F for the individual half-cells with specially constructed Mercury-Mercuric Oxide reference electrodes. The effects of plate spacing, electrolyte concentration, and separator materials on cell performance and charge retention were determined by constructing cells of the "Sandia" type. These cells had a nominal capacity of five ampere-hours.

The solid reaction products on the cell electrodes were found to be  $\text{Ni(OH)}_2$  and  $\beta\text{NiOOH}$  on the Nickel electrode and  $\text{Cd}$  and  $\text{Cd(OH)}_2$  on the Cadmium electrode. The active materials of the Nickel Electrode were in solid state solution.

The overall reaction in the Nickel-Cadmium cell was found to be



The potentials of the cells were lowered by increasing the concentration of the potassium hydroxide electrolyte, mainly because of the decreased activity of water. The positive (nickel) electrode had a negative coefficient of voltage change with temperature. This effect was much larger than that observed with the negative electrode and determined the overall effect of temperature upon cell voltage.

The Heat of Reaction for the cell was calculated from the slope of a plot of  $E/T$  versus the logarithm of the vapor pressure of water, and was found to be  $-62$  Kcal per gm. mole.

4201. Bourgault, P. L.

University of Ottawa, (1962)

### Studies on the Nickel Hydroxide Electrode.

Appears in Can. J. of Chem. (See Refs. 902, 903, 904 for abstracts).



## UNIVERSITY DISSERTATIONS (Cont.)

4202. Nagy, G. D.

University of Toronto, (1964)

### The Anodic Behaviour of Silver in Aqueous Solutions of Potassium Hydroxide.

Extensive data covering a range of temperatures have been obtained for the anodic behaviour of silver in a 1N. aqueous solution of KOH. Some studies of the reduction process for the same electrolyte were also made. For constant current anodic polarization, the following features are observed: (a) a low initial overpotential for  $\text{Ag}_2\text{O}$  formation until the film reaches a critical thickness which is of the order of 1000Å; (b) a rapid increase in the electrode potential at the critical thickness, going through a maximum; (c) a decay of the potential from this maximum to a potential somewhat above that for oxidation of  $\text{Ag}_2\text{O}$  to  $\text{AgO}$ ; (d) a further increase in the potential accompanied by oxygen evolution when most of the  $\text{Ag}_2\text{O}$  is converted to  $\text{AgO}$ .

The present study centered mostly around the formation of  $\text{Ag}_2\text{O}$  and the electrode behaviour in the critical film thickness region. It has been shown for the first time that the critical film thickness is a linear function of the logarithm of the formation current density. Once the critical thickness has been reached (or slightly exceeded) however, a reduction of current density does not permit a significant further thickening of the film to take place. The results of the potential decay measurements are complex, but the conclusions may be briefly summarized as follows: Most of the so called overpotential in the  $\text{Ag}_2\text{O}$  formation region is probably not true overpotential, but arises from the formation of the  $\text{Ag}_2\text{O}$  film in a high free energy state, presumably caused by the presence of defects. This potential appears to increase proportional to the logarithm of the formation current density, and decays over a period of the order of 8 hours. The residual overpotential in this region is too small for accurate analysis.

4203. Labat, J.

University of Bourdeaux, (1964)

### A Contribution to Research on Nickel Hydroxides.

Appears in *Annales de Chimie* 9, 399, (1964) (See Ref. 601, for abstract)

4204. Yohe, C. D.

Western Reserve, (1967)

### Electrochemical Processes on Nickel Oxide.

The objective of this thesis research has been to study the electrochemical properties of compound semiconductors. Anhydrous  $\text{NiO}$  has been chosen because 1) it affords an opportunity to examine charge transfer between ionic solution phase species and a semiconductor with rather localized carriers corresponding to controlled valency states, 2) extensive work has been reported in the literature for this oxide in conjunction with gas-solid catalysis studies and 3) this oxide is of importance in fuel cell and corrosion studies.

In summary the electrochemical properties of semiconducting nickel oxide are in many ways similar to those found with other p-type semiconductors.



## UNIVERSITY DISSERTATIONS (Cont.)

4205. Webster, Jr., W. H.

American University, (1967)

### Design and Development of a Continuous Flow Calorimeter and Measurements of the Thermal Characteristics of Nickel Cadmium Batteries.

This thesis discusses the design and development of an isothermal continuous flow calorimeter capable of measuring the thermal characteristics of batteries undergoing typical orbital cycling. The calorimeter was calibrated over the range of 0.10 to 1.00 watt, a range characteristic of the thermal output of a six ampere-hour nickel-cadmium battery. The thermal response was found to be linear in this range and the instrument was sensitive to 0.01 watt.

A Gulton six ampere-hour nickel-cadmium battery complete with an Adhydrode control electrode was subjected to three hundred twenty-two cycles using various rates of recharge and depths of discharge.

The enthalpy changes ( $\Delta H$ ) corresponding to the reactions occurring during the charge and discharge processes were calculated from the thermal data. These values obtained experimentally were in excellent agreement with the literature values for these reactions.

4206. Caulder, S. M.

Polytechnic Institute of Brooklyn, (1968)

### Thermodynamic Properties of the Nickel-Cadmium Alkaline and Lead-Lead Oxide Acid Cells.

An investigation of the nickel-cadmium electrochemical cell reaction using calorimetry, differential thermal analysis (DTA) thermogravimetric analysis (TGA) and X-ray analysis has shown that the previously believed independence of the electrochemical cell reaction on electrolyte type is not completely valid. The enthalpy change for the nickel-cadmium cell cycled in 7.9N KOH was found to be 33.2 Kcal. equiv.<sup>-1</sup> while that of the same cell cycled in 6.3N LiOH was 37.7 Kcal equiv.<sup>-1</sup> This enthalpy difference is attributed to a difference in the degree of hydration of the active material which is believed to be associated with the alkali metal cation.

DTA and TGA results were consistent with the calorimetric results which indicated that the active material cycled in LiOH was hydrated to a lesser degree than that cycled in KOH.

The temperature at which the two DTA peaks of the oxidized active material reached an endothermic maximum was found to be dependent on the alkaline hydroxide in which the active material was cycled. The reduced active material also gave endothermic dehydration and dehydroxylation peak. However, these peaks were independent of the electrolyte in which the active material was cycled.

X-ray analysis of the oxidized active material cycled in various alkali hydroxides showed no new compound formation, such as the lithium nickelate. However, new minor diffraction peaks were observed when the diffraction patterns of the oxidized active material cycled in LiOH was compared with those of the active material cycled in KOH.

Electrochemical cells fabricated with nickel electrodes containing coprecipitated didymium hydroxide with nickel hydroxide gave similar results with respect to electrochemical capacity and enthalpy change as those cells containing only active nickel hydroxide.



**PART V**  
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